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THE RELATIVE VALUES OF THE MITSCHERLICH AND HYDROFLUORIC ACID METHODS FOR THE DETERMINATION OF FERROUS IRON.[1]

BY W. F. HILLEBRAND AND H. N. STOKES.

Received July 27, 1900.

AMONG determinations in mineral and rock analysis, upon the accuracy of which great stress is laid, is that of iron in the ferrous condition. It is of special importance because an error attaching to it affects in like degree but opposite direction the ferric iron that is also nearly always present. Up to about the year 1867, the only method for its determination giving at all satisfactory results was that of A. Mitscherlich,[2] depending on the decomposition of the mineral at high temperature by rather strong sulphuric acid (3 parts acid to 1 part water by weight) in a sealed tube from which air has been expelled, and subsequent titration of the ferrous iron by permanganate. When pure hydrofluoric acid became a commercial article, the above method gave place in large measure to one depending on the decomposition of the silicate by a mixture of dilute sulphuric and hydrofluoric acids at atmospheric pressure and a tempera-

1 Published by permission of the Director of the United States Geological Survey.

2 *J. prakt. Chem.*, 81, 116 (1860).

ture not above 100° C., care being taken as before to prevent contact with air.[1]

It became known in the laboratory of the United States Geological Survey fully twelve years ago that the two methods generally give discordant results when applied to the same rocks, the Mitscherlich method in such cases always showing the higher figure for ferrous iron. With low percentages of iron the discrepancies were not very great, but they seemed, in general, to increase as the ferrous oxide rose, until, with a rock showing 10 per cent. ferrous oxide by the hydrofluoric acid method, the Mitscherlich method might give 12 per cent. Experiments with artificial ferrous salts threw no light on the subject, for both methods gave with them the same sharp and concordant results.

Until very recently no cause suggested itself whereby the discordance could be explained. In theory, the Mitscherlich method seemed perfect, and it was concluded that, given entire decomposition of all ferruginous minerals, the determinations made by it were nearer the truth than those by the hydrofluoric acid method. That the reverse is true in most cases, appears as the result of work done in this laboratory in an entirely different connection.

In the first place, it had been found by long experience that nearly all rocks carry small amounts of sulphides—pyrite, pyrrhotite, or both—often visible to the eye, but more often in such small amount as to escape direct observation. One of us (Stokes), in an investigation now in progress on the oxidizing action of ferric salts on sulphur, pyrite, and other sulphides, has found that this action is vastly more rapid and complete than has hitherto been suspected; that not only is the metal of the sulphide oxidized, but the sulphur to sulphuric acid as well.

The application of these observations to rock analysis shows that the presence of 0.01 per cent. of sulphur in any unoxidized form may produce a maximum error of 0.135 per cent. in the ferrous oxide determination and the not infrequent amount of 0.10 per cent. of sulphur will multiply this error by 10. One atom of sulphur (32) requires for its complete conversion into trioxide the oxygen of three molecules of ferric oxide (480), which then becomes six molecules of ferrous oxide (432). The

[1] J. P. Cooke: *Am. J. Sci.* (2), 44, 347 (1867).

case is still worse with the sulphide, since not only the sulphur, but its accompanying metal must be oxidized. The above percentages of sulphur evolved as hydrogen sulphide and fully oxidized would involve errors in the ferrous oxide determination of 0.18 per cent. and 1.80 per cent., respectively. The error caused by sulphides tends to become greater the more there is present of either or both sulphide or ferric salt. Now the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively rich in pyrite and pyrrhotite ; hence the increased discrepancy between the results by the two methods, as the iron contents of the rock rise, is fully in accord with the above explanation.

The following experiments made by Stokes (somewhat out of their contemplated order in his investigation referred to) bear out the above statements most fully and show that the Mitscherlich method for rocks and all minerals which contain even a trace of free sulphur or sulphides is no longer worthy of a moment's consideration.

Experiment 1.—0.0010 gram pyrite was heated with 25 cc. of a sulphuric solution (1 part acid to 3 parts water by weight) of ferric ammonium sulphate (0.0470 gram of ferric oxide) in a horizontally-lying sealed tube for six hours at 175° to 195° C. All air had been carefully replaced by carbon dioxide. The pyrite had nearly disappeared, and titration with permanganate showed a consumption of oxygen equivalent to 0.0068 gram ferrous oxide. Complete oxidation of the pyrite would have required oxygen equivalent to 0.0090 gram ferrous oxide.

Experiment 2.—This was exactly like the first, except that 0.0013 gram pyrite was used. Permanganate was reduced equivalent to 0.0090 gram ferrous oxide. Had oxidation been complete the figure would have been 0.0117 gram.

It is quite possible that in both of these experiments the oxidation would have been complete had the pyrite been disseminated throughout a greater space in the tube, as is the case when rocks and minerals are treated, because of the presence of a gram or thereabouts of diluting quartz and silicates.

Had precisely similar experiments been made with rock powders carrying 0.10 per cent., and 0.13 per cent., of pyrite with

4.7 per cent. of ferric oxide and no ferrous oxide, the following erroneous results might have appeared:

	I.	II.
Ferrous oxide.....	0.68	0.91
Ferric oxide.....	4.00	3.76

To overcome the possible objection that the foregoing experiments were not conclusive as to the worthlessness of the Mitscherlich method in presence of sulphides because the concentration of the acid was very different from the normal, the following sealed tube experiments were made with acid of the normal strength (3 parts acid to 1 part water by weight) without any ferric salt, the belief being that the stronger acid, under the conditions of the experiment, would itself act as an oxidizer.

Experiment 3.—Pyrite 0.0016 gram. Three hours at 195° C. Solution only partial. Consumption of permanganate equivalent to 0.00117 gram ferrous oxide.

Experiment 4.—Pyrite 0.0032 gram. Twelve hours at 220° C. Solution perfect. Odor of sulphur dioxide apparent on opening tube. Consumption of permanganate equivalent to 0.01742 gram ferrous oxide.

Experiment 5.—Sulphur 0.0021 gram. Three hours at 195° C., and, as the sulphur had not disappeared, further six hours at 250° C. Entire disappearance of the sulphur. Consumption of permanganate equivalent to 0.01320 gram ferrous oxide.

Experiment 6.—Sulphur 0.0039 gram. Twelve hours at 220° C. Entire disappearance of the sulphur and strong odor of sulphur dioxide on the opening tube. Consumption of permanganate equivalent to 0.03619 gram ferrous oxide.

In experiments 4, 5, and 6, where decomposition was complete the consumption of permanganate is considerably less than theory requires, but this is explained by the escape of not a little sulphur dioxide on opening the tube. Had a ferric salt been present the consumption of permanganate would undoubtedly have reached that required by theory.

It might be supposed from the foregoing that a similar error would affect ferrous iron determinations by the hydrofluoric acid method. However, experiment has shown that with the amounts of sulphide usually found in igneous rocks their effect is negligible, though by increasing the amount of sulphide the

effect becomes more and more apparent because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand,—a temperature of 150°–200° C., and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed,—the sulphur of the sulphides becomes nearly, if not quite, fully oxidized to sulphuric acid, at the expense of the ferric oxide in the rock, with the production of an equivalent amount of ferrous oxide in addition to that resulting from the iron of the sulphide itself.

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron estimation by the hydrofluoric acid method, the following tests were recently made by one of us.

Part of a fine crystal of pyrite was rather finely powdered and boiled out with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, or from superficial oxidation of the powder, since a second boiling with fresh acid afforded a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it, when treated with dilute sulphuric and hydrofluoric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but two drops of a permanganate solution representing only 0.0032 gram ferrous oxide to the cubic centimeter.

That the error obtaining under the conditions prevailing in rock analysis might be ascertained, successive portions of one gram each of a hornblende schist free from sulphur and carrying 10.09 per cent. ferrous oxide as the mean of several determinations and 4 per cent. ferric oxide, were mixed in a 60 cc. platinum crucible with 0.02, 0.025, and 0.10 gram, respectively, of the above purified pyrite powder. This mixture was then treated with hydrofluoric and sulphuric acids as above, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end-reaction by

its reducing effect upon the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent. ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time, it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink color produced by an excess of permanganate. If much ferrous iron be present, many cubic centimeters of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown color characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

WASHINGTON, July, 1900.

ON THE DIGESTION AND ASSIMILATION OF PENTOSES AND FURFUROIDS.

BY C. F. CROSS, E. J. BEVAN, AND J. S. REMINGTON.

Received July 16, 1900.

THE furfural-yielding constituents of plant tissues continue to be designated by the majority of observers as pentosans. It is probable, however, that the group of natural products thus constituted are of more varied characteristics.

It must be noted first that we have no specialized form of pentosane comparable with starch and that the substances described as such are products isolated by chemical processes in the laboratory and devoid of the well-marked individuality and properties of the hexose-anhydride. We are not aware of any

evidence upon which the individuality of the best known of the reputed pentosanes, *viz.*, "Holzgummi," has been finally established.[1] Generally this group of substances is investigated in terms of furfural, obtained by boiling with condensing acids; and the relation of this aldehyde to the pentoses is indirect and of course not exclusive. Several of the now well-known oxidized derivatives of the hexose-carbohydrates are similarly condensed to furfural; of these we can call to mind: (*a*) Glycuronic acid; (*b*) the osones or ketoaldoses obtained by Fischer from the osazones and more recently and directly by ourselves by the action of hydrogen peroxide on the hexoses;[2] (*c*) a number of imperfectly defined products of oxidation of the hexoses and their polyanhydrides obtained both by laboratory and natural processes.[3]

Lastly it must be noted that investigation has failed to identify the pentoses as such occurring in the plant and the conclusion generally accepted at this date with regard to their formation is that they are not direct products of the assimilation process but originate from hexoses by processes of oxidation or internal change.[4]

Complementary confirmation of the exceptional physiological relationships of the pentoses is also supplied by the facts (1) that they are entirely resistant to alcoholic fermentation (yeast) and (2) are not assimilated by animal digestion.

From this brief résumé of the present state of our knowledge we draw the following conclusions: (*a*) That the group of furfural-yielding constituents of plants may comprise in addition to petosans, oxy-hexoses (respectively anhydride) representing intermediate terms of a complex hexosan-pentosan series; and in view of this probability we prefer as a group designation the term furfuroid, and (*b*) that such oxyhexoses may yield to yeast fermentation and to animal assimilation.

Since these furfuroids are constituents of cellular tissues the question of alcoholic fermentation can only be studied by way of the products of acid hydrolysis. In so far as these products are pentoses they resist fermentation. This has been finally

[1] "Kohlenhydrate," II, p. 202, Tollens.

[2] *J. Chem. Soc.*, **73**, 463 (1898); Morrell Crafts: *Ibid.*, **75**, 786 (1899).

[3] *Ber. d. chem. Ges.*, **27**, 1061: Krüger and Tollens: *Ztschr. angew. Chem.*, 1896, Heft 2.

[4] "Kohlenhydrate," II, p. 60.

established by the very careful investigation of Tollens;[1] at the same time we and other observers have studied cases of yeast fermentation in which there has been a considerable disappearance of the furfuroids from solutions in which they exist in a more or less fully hydrolyzed form.

In his investigation of this result Tollens arrives at the conclusion that the disappearance of the furfuroids is accompanied by the appearance of acid products; also that this effect is not inconsistent with the view that the products reacting in this way are pentoses.[2] Still the question is by no means finally elucidated and the incompleteness of the present solutions of the problem involved should be recognized.

In regard to the problem of animal digestion and assimilation we have to notice the results of investigation from two points of view. The pentoses proper have been investigated by Ebstein[3] who found that xylose is not assimilated, being voided in unchanged form in the urine and Salkowski[4] whose observations on arabinose led to the following conclusions: "Von dem jeden Thiere eingegebenen 10 g. Arabinose wurde etwa 1/5 unverändert durch den Harn ausgeschieden: das Blut enthält wenig, die Muskeln reichlich Arabinose. In der Leber fand sich gewöhnliches Glykogen und nicht, wie gehofft ein Pentosan. Die Resorption der Arabinose erfolgt schnell u. vollstandig."[5]

On the other hand the furfuroids of fodder plants have been investigated by a number of observers who have variously estimated the proportion digested at from 40–90 per cent. These numbers represent for the most part the percentage ratio of the furfuroids disappearing in the digestive process, but they do not attempt to deal with the further question of assimilation. This more elaborate problem has recently been solved in a typical case by O. Kellner and A. Kohler.[6] Oxen were fed upon a rye straw which had been previously extracted by boiling with alkaline lye—the product containing:

78.6 per cent. Rohfaser with
31.1 per cent. Furfurol gebende substanz.

[1] Stone and Tollens: *Ann. Chem.* (Liebig), **249**, 257; Tollens: *J. Fed. Inst. Brewing*, 1898, 451.

[2] Tollens: *Ibid.*

[3] *Archiv. Pathol. Anat.*, **129**, 401.

[4] *Central bl. Med. Wiss.*, 1893, No. 11.

[5] *Ber. d. chem. Ges.*, 1893, 896.

[6] Landw. Vers. Stat., 1900, 53, 1, 474.

This product was added to the "Grundfutter" specially designed "zur Deckung des Mindestbedarfes des Thiers". The following results were obtained: Of the total product 95.8 per cent. was digested, and of the total available energy, 63.1 per cent. contributed to the formation of flesh and fat. The "furfuralgebende Substanz" contributed its proportion to the result and generally the cellulosic substance thus prepared has approximately the same feeding characteristics and value as starch.

But we find no records of investigations in which the furfuroids have been previously isolated by processes of acid hydrolysis. In absence of such results the proportions determined above are open to the objection that they are complicated by the unknown factor of digestive hydrolysis. To further elucidate the problem, therefore, we have carried out feeding experiments with the complex of products obtained from brewers' grains by digestion with dilute sulphuric acid (1 per cent. H_2SO_4) in an autoclave at a temperature of 130°. Under these conditions the furfuroids are selectively attacked and constitute 80–90 per cent. of the total soluble extract. The products in this form we have previously investigated and have found to be fully hydrolyzed from the numbers for cupric reduction; *viz.*, 110–120 (dextrose = 100) and yields of osazones.[1]

The acid extract is neutralized ($CaCO_3$), filtered and evaporated. On distillation with hydrochloric acid of 1.06 sp. gr., the extract yielded 39.5 per cent. furfural calculated to the total dry weight. To convert the product into a form in which it could be easily administered to the animal (rabbit) as a foodstuff, it was mixed with a strong solution of gelatin at 20° C. and then with sufficient bread to give, when cold, a solid granular product. With this artificial food was associated a due proportion of fresh vegetable food; *viz.*, carrot and cabbage. The experiments were conducted with the usual precautions, in parallel series, one animal receiving the diet as above, a second receiving this same diet less the artificial furfuroid constituent. The details of the experiment are published elsewhere and need not be reproduced here.[2]

[1] *J. Chem. Soc.*, 1897, 1001–1010.

[2] *J. Soc. Chem. Ind.*, 1900, April 30.

The results obtained established the following high proportion (per cent.) of digestion and assimilation of the total furfuroids of the mixed diet

96.4 98.4 97.3 96.4 94.5

which are certainly minimum numbers for the special group of furfuroids under investigation. No pentoses or other furfural-yielding products were present in the urine, which was examined from time to time.

It may be concluded from these results that the typical furfuroids of cereal tissues when fully hydrolyzed are digested and assimilated by the herbivera as completely as starch and its products of hydrolysis. In this respect they differ from the pentoses and their anhydrides.

In view of these results and the exceptional physiological history of this group of constituents of plant tissues, which is by no means fully elucidated, we consider the term "furfural gebende substance," or more shortly "furfuroid" is to be preferred as a general designation, reserving the term pentosan for its strict use; *i. e.*, as applied to a pentose-anhydride ($H.C_5H_{10}O_5—MH_2O$).

4 NEW COURT, LONDON, AND LANCASTER,
ENGLAND, May 10, 1900.

ESTIMATION OF PYRRHOTITE IN PYRITES ORE.

BY F. B. CARPENTER.

Received August 15, 1900.

SINCE the introduction of pyrites into the manufacture of sulphuric acid, industrial laboratories have been frequently called upon to make analyses of pyrites ores to determine their quality for manufacturing purposes. In order to determine the relative value of these ores it is not only necessary to determine their sulphur content, but it is also essential that an estimation be made of those sulphides, which are difficult to decompose in the furnace. Fairly satisfactory methods have been described for the determination of zinc, arsenic, copper, etc., but I have heretofore seen published no satisfactory methods for the estimation of pyrrhotite. It is well known by acid makers that it is difficult to get the sulphur from this material, especially in lump burners, and as it is contained in nearly all our domestic ores to

a greater or less extent, the importance of its presence should not be overlooked.

The usual method for the determination of pyrrhotite in pyrites is based on its magnetic properties, and briefly stated, is carried out as follows: About 25 grams of the material, ground to pass a 60-mesh sieve, is spread out on a piece of glazed paper, and a magnet of the horseshoe type is passed backward and forward through small portions at a time. As soon as the poles of the magnet are loaded with attracted material the bridge between them is broken down with the armature, so that as much of the mechanically retained pyrites as possible may be dislodged; then after striking the magnet several times sharply with the bare hand to further free the magnetic portion from the pyrites, the adhering substance is transferred to a clean sheet of paper; then another portion of the ore is treated like the first, cleansing and transferring the attracted part in the same way, and this continued until the whole amount has yielded all magnetic matter. The portion removed to the second paper is still far from pure, and the cleansing operation is repeated for a second and third time in the same manner as the first, except that the magnet is held at a sufficient distance to lift the material and not rub among the particles. The magnetic material thus obtained is weighed and sulphur determined in one-half to one gram. The percentage of sulphur existing as pyrrhotite is then calculated from the results by multiplying the percentage of magnetic material found in the ore by the amount of sulphur found in 1 gram of the same. The difficulties in working this method are no doubt apparent to all who have used it. Pyrrhotite is only slightly magnetic and is very difficult to separate from the non-magnetic ore. After following out the method just described with the greatest care it is impossible to remove all the pyrrhotite or to have the magnetic material free from pyrites. We have slightly improved the method in this laboratory by substituting the electromagnet for the ordinary style, but the results are still far from satisfactory.

The method which I am about to describe was worked out in this laboratory, and is based on the solubility of the two sulphides (FeS_2 and Fe_7S_8) in hydrochloric acid, FeS_2 having been found to be practically insoluble while Fe_7S_8 seems to be wholly decomposed.

Details of the Process.—Determine total sulphur and silica by the usual methods; also copper, zinc, etc., if they are present in appreciable amounts. Test for pyrrhotite with magnet, and if present proceed as follows:

Treat 2 grams of the sample (ground to pass a 100-mesh sieve) in an 8-oz. beaker, covered with a watch-glass, with 30 cc. concentrated hydrochloric acid, boil ten minutes, filter on a weighed Gooch crucible, wash successively with warm dilute hydrochloric acid, hot water, alcohol, and finally several times with small portions of carbon disulphide. Dry at 100° and weigh. Weight of residue = $FeS_2 + SiO_2$. $(FeS_2 + SiO_2) - SiO_2 = FeS_2$. The sulphur required to satisfy the iron in the resulting FeS_2 is subtracted from the total sulphur, and the remaining sulphur calculated to Fe_7S_8 (pyrrhotite). The details of the calculations are as follows: $FeS_2 \times 0.534$ = sulphur in FeS_2; subtract this from the total sulphur and multiply the result by factor 2.529; this gives the percentage Fe_7S_8 present in the ore. These calculations apply to ores containing only traces of other metals besides iron. If other metals are present in appreciable amounts due allowance will have to be made. Zinc sulphide will be practically all decomposed by the hydrochloric acid; the percentage of zinc found, will therefore have to be satisfied with the required amount of sulphur, and the sulphur thus used deducted from the total sulphur before other calculations are made. Chalcopyrite, on the other hand, is only partly decomposed by the treatment with hydrochloric acid. Thus for the accurate estimation of pyrrhotite it will be necessary to make copper determinations both in the residue and filtrate, and calculate the results to chalcopyrite, subtract the amount of chalcopyrite found in the residue from the total residue, and the amount of sulphur required to satisfy the percentage of copper in the filtrate from the total sulphur before making the calculations. If only a small percentage of copper is present with no other metals, approximate results may be obtained by using dilute acid (1 to 1) for treating the ore. The amount of copper dissolved out by this treatment will be so small that it may be overlooked in the determination. The whole percentage of copper in the ore is in this case calculated to $CuFeS_2$, and deducted from the total residue. Copper may be determined very quickly and

accurately by the cyanide process as described by Ricketts and Miller. If other disturbing factors are present the method will have to be modified accordingly, but the method as described gives results sufficiently accurate for all practical purposes on the great majority of commercial pyrites ores. This process is simple, reasonably quick, and gives much more satisfactory results than the other methods we have tried.

Mr. S. H. Sheib who is connected with this laboratory has rendered valuable assistance in perfecting this method of pyrrhotite determination, and its success is largely due to his careful work.

LABORATORY VIRGINIA-CAROLINA CHEMICAL CO.,
August 1, 1900.

THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK.[1]

BY JOSEPH F. GEISLER.

Received August 8, 1900.

CONDENSED milk, as its name indicates, is a more or less concentrated milk, prepared by evaporating or distilling off a large percentage of the water of the milk. The concentration is usually carried to a degree to meet popular taste and trade requirements, unless the law establishes a specified degree of condensation. Broadly, this class of milk may be divided into the sweetened and unsweetened condensed milk, the former containing a large per cent. of cane-sugar as sweetener and preservative. Aside from its general good qualities, the extreme precaution of cleanliness in the preparation of most of the condensed milks has added much to their popularity, so that the sale and consumption of these milks is assuming vast and rapidly increasing proportions. As an article of food it is therefore more frequently being made the subject of analytical inquiry to determine its quality and freedom from adulteration.

While certain manufacturers pride themselves in turning out a product of uniform color, consistency, and superior keeping qualities and purity, others have deliberately put adulterated goods on the market and were prosecuted and fined for the same.

The analysis of ordinary milk presents no particular difficulties

[1] Read at the Twenty-first General Meeting of the American Chemical Society, June, 1900.

to the experienced analyst, but there is an abundant and cumulative evidence to show that the correct analysis of sweetened condensed milk is difficult and has proved to be a stumbling block to the efforts of many chemists.

Thus, quite recently, an article "A Method of Analysis for Canned Condensed Milk,"[1] by F. S. Hyde, appeared as a "Contribution from the Havemeyer Laboratories of Columbia University, No. 6," and this article has obtained wide circulation.

The results of the analyses of the first 17 samples reported are so utterly out of harmony with the composition of commercial condensed milk that experienced analysts have only to refer to the method whereby the results were obtained to learn the cause of the faulty statements. It is the general experience that the easiest part of analytical work is the writing out of a method. Without going into the details of the article referred to, I would quote[2] the following, which has a decided bearing in the application of the food laws:

A law of New York State requires that no "condensed milk shall be made,—unless the proportion of milk solids shall be in quantity the equivalent of twelve per centum of milk solids in crude milk and of which solids twenty-five per centum shall be fats." Sec. 25, Chap. 143, L. 1894.

"Generally the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

"The original cow's milk used may be considerably above the legal standard and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions the manufacturer might be liable to prosecution, although the product might be perfectly wholesome."

In the writer's experience it is the rare exception rather than the rule for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids.

If, as stated, milk above the standard required by law be used

[1] This Journal, **21**, 439 (1899).
[2] *Ibid.*, **21**, 444 (1899).

for the condensation, there could be no legal prosecution of a manufacturer since the concentration would not materially alter the ratio of fat to milk solids, and the section of law quoted does not define the degree of concentration. Therefore, whether condensed little or much, the "condensed" product would not be an infraction of the law quoted, and prosecution under the same is out of the question.

Aside from insufficient condensation, it is generally assumed that skimming or the removal of butter-fat is the principal temptation to defraud on the part of the manufacturer. To prove skimming, the first essential is the accurate estimation of the fat, assuming the per cent. of fat obtained to be butter-fat. That is to say, the mere finding of the required per cent. of fat, and ratio of fat to milk solids would not prove such milk unadulterated unless the fat found was actually butter-fat.

Attempts have been made to remove the butter-fat and substitute other fat for the same in condensed milk; hence, the allusion to butter-fat particularly.

In the unsweetened condensed milk the estimation of the fat presents no particular difficulty, especially since the introduction of the Adams' coil method,[1] when the necessary precautions are taken. The large surface over which the milk solids are spread in the paper, a minimum of 110 sq. in., offers a medium from which solvents ordinarily rapidly extract[2] the fat.

The coil method has found general favor among analysts and were it not for the inconvenience of preparing "fat-free" coils it would be *par excellence*, and with certain modifications, the best method for the purpose. The preparation of the coils is tedious, but where accuracy is required the previous extracting of the coils to be used must be resorted to, as the quality of paper varies, some lots containing considerably more extractable matter than others.

Chemists were quick to avail themselves of the advantages of the coil method and use it in the estimation of fat in sweetened condensed milk, for the large surface offered advantages to overcome the difficulties experienced and pointed out by Hehner,[3]

[1] *Analyst*, March, 1885.

[2] See Vieth: *Analyst*, 16, 127; Geisler: "The Relative Merits of the Wanklyn and the Adams Methods in the Estimation of Fat in Milk Analysis," this Journal, 12, 488-500.

[3] *Analyst*, 4, 45 (1879).

who stated "that it is quite impossible to extract the fat from the total solids by means of ether, or benzoline, the large amount of cane-sugar effectually protecting the fat."

Adams' method was not available until some years later. In the light of recent published analyses of sweetened condensed milk, Hehner was a "martyr" considering the abuse heaped on him by the manufacturers for the analyses, for it will presently be shown that even the extreme advantages of the *coil method*, unless certain precautions are taken, has its pitfalls. In the application of the coil method it is customary among a large number of chemists to proceed as follows: Thus Cornwall[1] and Wallace[2] state in following out the method:

"Rather thick, white filter-paper was thoroughly extracted with ether in a Soxhlet apparatus and 5 cc. of the diluted milk (equal to 2 grams of the condensed milk) dropped on a nearly square strip of this paper[3] large enough to conveniently soak up the milk. To avoid the formation of candied spots the milk was uniformly spread over the paper by brushing with a small narrow strip of the same kind of paper. After drying in the air the paper was rolled into a loose cylinder and dried in the air-bath at 100° C. for about an hour and a half.

"The fat was then extracted with ether, for two hours, in a Soxhlet apparatus, and a second extraction was made, lasting for an hour to an hour and a half longer. The second extraction usually yielded less than 4 milligrams more of fat, and often none at all. The fat determination was made in duplicate. The greatest difference was 0.2 per cent., usually only a hundredth of a per cent."

In brief, the Adams' method, as applied to sweetened condensed milk, consists in transferring about 2 grams of milk diluted to 5 or 6 cc., to a paper coil of 50–60 sq. in. (100–120 sq. in. of surface, both sides), and extracting the fat by means of ether or petroleum ether.

The quantity of milk taken for the extraction is not a matter

[1] Cornwall: Rep. Dairy Com., N. Y. State, 1890, p. 408; N. J., 1887.

[2] Wallace: Rep. Dairy Com., N. J., 1899, pp. 43-47.

[3] Cornwall: Rep. Dairy Com., N. J., 1891, p. 90; filter-paper of medium thickness 10 × 5 inches. Wiley: Rep. Dairy Com., N J., 1891; thick filter-paper strips 24 × 2½ inches.

of indifference, nor is the solvent, or the method of extraction. Unless the ether is dry and free from alcohol, the coils get too soggy to permit the full extraction of the fat. Even with dry ether or petroleum ether, losses may occur even as high as 0.5 per cent. as against an occasional maximum of about 1 per cent. in a direct extraction. Evidence of this may be obtained by treating the thoroughly exhausted coil after drying, to a thorough soaking in water until all soluble matter is removed, drying the coil, and again exhausting with ether or petroleum ether, when additional fat will be found in the majority of cases.

Direct exhaustion by ether for four hours leaves variable percentages of fat in the residuum on the coils. This is true of other solvents as well. If 2 grams of the condensed milk are used per coil, the coil, after the first exhaustion, which presumably should yield all the fat, should be dried and exhausted with water, again dried and exhausted with the volatile solvent. Forty-nine separate examinations showed differences for the second exhaustion of 0.27 to 1.2 per cent. of which nine ranged from 0.27 to 0.49 per cent.; twenty-three from 0.50 to 0.75 per cent.; and the remainder from 0.75 to 1.2 per cent. That is to say, if the precaution of exhausting the coils with water had not been taken, the fat in the milks would have been underestimated from 0.27 to 1.2 per cent. in actual per cent. of fat by the coil method.

The large variation is due principally to the varying per cent. of cane-sugar in the different samples. As the time of extraction for these varied from two and a half to four hours for the first extraction, a separate set of extractions under fixed conditions was made. The coils (filter-paper strips 22 × 2.5 inches, were "alcohol-ether" coils, and each coil again exhausted for five hours with the solvent with which it was to be subsequently treated. Simple exhaustion of the coils by ether alone does not remove all the extractable matter from the same. The extractive matter obtained for the eight individual coils varied from 1 milligram to a maximum of 2.5 milligrams. The latter was extracted by petroleum ether from a coil not previously treated with this solvent.

The eight coils were therefore free from extractable matter. Two were taken to be extracted with petroleum ether, and two with a mixture of petroleum ether (15 per cent.) and ethyl ether. The first extraction lasted three hours and the second two hours.

After the first three hours' exhaustion, the coils were taken out and dried, and then exhausted with water until all soluble matter was removed. The coils were again dried and again subjected to their respective solvents for two hours. The results obtained were as follows:

PETROLEUM ETHER.

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0355	First extraction.....	0.160	7.86
	Second "	0.013	0.63
			8.49
2.0815	First extraction.....	0.158	7.59
	Second "	0.015	0.72
			8.31[1]

"ETHER-PETROLEUM" ETHER.

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0645	First extraction.....	0.156	7.55
	Second "	0.017	0.82
			8.37
2.035	First extraction.....	0.1605	7.88
	Second "	0.012	0.58
			8.46

Results by taking about 1 gram of milk and treating as above:

1.0235 grams taken gave 0.0854 gram fat or 8.35 per cent.
1.084 grams taken gave 0.0917 gram fat or 8.46 per cent.

Direct exhaustion with petroleum ether for five hours for the first exhaustion, and two hours further exhaustion after the water treatment, gave:

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0395	First extraction.....	0.159	7.795
	Second "	0.0135	0.661
			8.456
2.013	First extraction.....	0.155	7.699
	Second "	0.0155	0.769
			8.468

The actual time limit will not in all cases do justice to extraction where petroleum ether is used to any extent, as the siphonings are

[1] Water slightly milky, indicating loss of fat.

not always regular. Anhydrous ether, *i. e.*, water-washed ether shaken with concentrated glycerine and redistilled after separation has taken place, shows differences as great as those. The mixture of petroleum ether and ethyl ether was a water-washed ethyl ether mixed with 15 per cent. of petroleum ether prepared by thoroughly shaking and mixing the mixed ether with about 25 per cent. of concentrated glycerine and redistilling the thoroughly separated ether mixture. Coils treated with an anhydrous ether are usually quite crisp when taken out of the extraction apparatus.

Chemists who have made comparative tests have no doubt found that 1 gram of the condensed milk per coil will usually yield all the fat to within 0.2 to 0.3 per cent. on four or five hours' extraction with petroleum ether, or dry ethyl ether, or a mixture of ethyl and petroleum ether, and that the loss rarely exceeds 0.2 per cent.

The amount of milk[1] used per coil is quite a variable one among chemists.

The method of taking a sample and transferring it to the coil may be minor details but important as to possible variation in results by the coil method. While the quantity of original milk will be noticed to vary from 0.5 to 2 grams per coil, it must be apparent that the margin of safety may be overstepped in either direction, for while the maximum quantity may be too large for complete direct extraction, the minimum quantity is too small, as a difference of 1 milligram in fat obtained represents at once 0.2 per cent. For the general run of fat estimation, little fault will be found with results obtained by exhausting the fat from 1 gram of the condensed milk from a *fat-free* coil by the direct exhaustion for four to five hours with petroleum ether, or ether-petroleum ether.

Accuracy in fat estimation to within 0.2 per cent. in sweetened condensed milk is certainly attainable where the necessary precautions are taken. Where 2 grams of the condensed milk are taken the results cannot be depended upon, however, as repre-

[1] T. H. Pearman and C. G. Moor (*Analyst*, **20**, 268) use 5 cc. of a 10 per cent. solution; A. H. Allen ("Commercial Organic Analysis," Vol. IV., 2nd ed., p. 235) recommends 5 cc. of a 10 per cent. solution; J. H. Shenstone (*Analyst*, **13**, 222) uses 2 grams; Wallace (N. J. State Dairy Com. Rep., 1899, pp. 43-47) uses 2 grams; Cornwall (N. J. State Dairy Com. Rep., 1887, 1890, p. 408) uses 2 grams; H. Throop Richmond and L. K. Boseley (*Analyst*, **18**, 170) use 5 cc. of a 15-30 per cent. solution.

senting the full yield of fat, unless the exhausted and dried coil is exhausted with water, and again exhausted with the volatile solvent. Water-washed ether mixed with 10 to 15 per cent. petroleum ether and distilled after shaking out with concentrated glycerine, answers the purpose as well as petroleum ether, as a solvent, and possesses other advantages if the petroleum ether has the proper boiling-point. The commercial petroleum ether is not suitable for this purpose, but suitable fractions of the same may readily be obtained on distillation.

The effective manner in which the cane-sugar prevents the action of the solvents upon the fat is well illustrated in the asbestos-tube method for fat estimation, in which 20 cc. of a 20 per cent. solution of the milk (4 grams) is deposited upon asbestos fiber, and, after drying, exhausted with petroleum ether. This method[1] has been the means of the unjust and unwarranted condemnation of quite a number of condensed milks. It has been proved that the method failed to exhaust all the fat, often 2 to 3 per cent. remaining in the residue, as has been amply demonstrated by exhausting the residue with water and recovering the shortage of fat in the residuum. The asbestos method has found favor in many quarters and was the direct cause of condemnation of pure milks in several instances.

The recurring frequency of unjust condemnation of condensed milk makes it particularly necessary for chemists to exercise great caution in expressing opinions upon whether a milk is skimmed or not. There are instances on record where sweetened condensed milks with high content of cane-sugar and of unquestioned purity were condemned as adulterated on the strength of the analysts finding low percentages of fat (3.8 per cent. lowest and a considerable number ranging from 5.5 to 6.8 per cent.) when more accurate methods demonstrated the presence of over 8 per cent. of fat in all the samples.

A difference of 0.5 per cent. fat has a very important bearing in the enforcement of a law defining the fat contents in milk solids. This is particularly true when the Ritthausen method is used for the estimation of the albuminoids, any error in the fat estimation reflecting its deficiency in increase of the albuminoids (the albuminoids being determined by difference) so that the

[1] Bulletin No. 54, Condensed Milk, Inland Revenue Department, Canada.

ratio between fat and albuminoid is distorted to a degree which would reflect seriously upon the milk under examination, and indicate probable skimming in the minds of some chemists.

This no doubt accounts for the discrepancy in quite a number of published analyses of the excess of albuminoid over fat in what probably were unskimmed milks. When such discrepancies are noticed in an analysis it is advisable to check the results by a nitrogen estimation by the Kjeldahl method, if this was not used in the first instance.

CONCLUSION.

In conclusion I would add that where as much as 2 grams of the sweetened condensed milk is used per "Adams' coil," the full extraction of the fats cannot be depended upon in a direct exhaustion of the coil by a four or five hours' treatment. For general usage 1 gram of milk per *fat-free* coil and four or five hours' exhaustion will give results which will rarely exceed the experimental errors common to complicated methods in which many minor details all must add their perceptible quota to a final result. The asbestos-tube[1] method, without water exhaustion, cannot be considered as giving acceptable results, as the shortage of fat by the same renders the results worthless. Three or four hours' exhaustion of the dried residue with petroleum ether, drying the exhausted mass and reexhausting with petroleum ether, will recover most of the fat.

The details of *modus operandi* especially as to proportion of milk taken to asbestos can no doubt be adjusted so that with the precaution of water exhaustion indicated the results will be fully as reliable as those by other methods. The many factors entering into any method for fat estimation in sweetened condensed milk would indicate that maximum variations of $\pm$ 0.1 are possible, and that any method yielding uniform results within that range would be acceptable for all ordinary purposes, as to accuracy.

[1] Bulletin No. 54, Condensed Milk, Inland Rev. Dep't, Canada.

A NEW COAL CALORIMETER.

By S. W. Parr.

Received July 24, 1900.

IN the study of combustibles and in all tests connected with fuels no data is of any value that does not go back to the thermal units involved. This fact itself is not new but its application, especially in technical work, has had a marked increase in recent years. This increase has come about in spite of, rather than because of, the instruments available for the determination of heat units. It is not necessary here to describe the difficulties and defects connected with existing calorimeters, more than to note perhaps the two extremes; *viz.*, the L. Thompson calorimeter on the one hand which admits of results varying by 15 per cent. from the truth, and the high pressure bomb on the other which, while accurate, requires an elaboration of apparatus and skill in manipulation not conducive to the wide use it deserves.

The calorimeter here described has the advantage of operating without an oxygen gas supply; its manipulation is simple and the extraction of the heat rapid, owing to the compact mass in which the heat is generated. It is especially adapted to soft coal and while designed for technical purposes its factor of error is well within 0.5 per cent., making its results, therefore, easily comparable with those obtained by the Berthelot or Mahler bombs. The principle involved in the process depends upon the liberation of oxygen from such a compound or chemical as shall in turn absorb the products of combustion thereby avoiding the necessity of providing conduits for the gases. A chemical which admirably meets these requirements is sodium peroxide. Its operation may be illustrated by the following experiment which was one of the first used to determine the adaptability of this chemical. A sample of combustible and sodium peroxide in suitable proportion were placed in a short, heavy, copper tube with close-fitting screw plugs at each end and the contents thoroughly mixed by shaking. The bomb was then held in the flame of a Bunsen burner till ignition was effected. Upon cooling and opening it was found that no pressure of gas was pres-

ent and on dissolving out the fused mass the combustion was shown to be complete. The instrument ultimately employed for utilizing these conditions may be best shown by an outline sketch.

A (Fig. 1) is a copper vessel of a little over two liters' capacity insulated by two outer vessels of indurated fiber, B and C, so

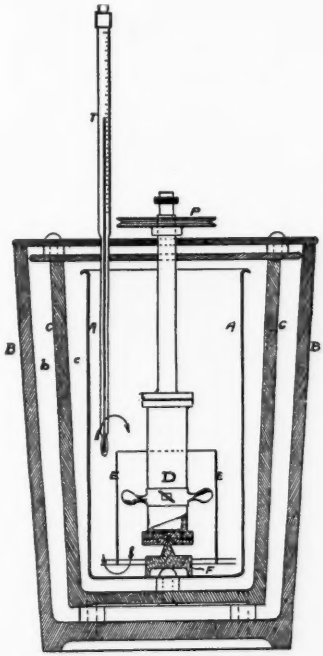

Fig. 1.

placed as to provide further insulation by the air spaces *b* and *c*. The cover is double to correspond with an air space between, the two parts being connected for convenience in handling. The cartridge D has an inside capacity of about 25 cc. It rests on a pivot below and extends through the covers above and has a small removable pulley at the end. Turbine wings fastened to spring clips are placed on the cartridge, and a short cylinder E, open at both ends, is provided for directing the current set up

by rotation of the vanes attached to the cartridge. The vanes are so set as to deflect the currents downward first along the cartridge and then up along the outside of the cylinder. The stem G of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 2). It is, moreover, provided with a valve D at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends B and C of the cartridge screw on. The process then is as follows: 1 gram of coal ground to pass through a 100-mesh sieve and dried in the oven as usual at 105°–110° is put into the cartridge, 16 to 18 grams of sodium peroxide are added, the top screwed on and the whole shaken to thoroughly mix the contents. The peroxide varies somewhat in fineness. It should practically all pass through a 25-mesh or 1 mm. sieve. After tapping the cartridge to settle the charge in the bottom, it is placed in the can and 2 liters of water added, the temperature of the water being 3° or 4° lower than the temperature of the work room. The pulley is connected by string to a small water or electrical motor giving about 50 to 100 revolutions per minute to the cartridge. When constant temperature is reached, the reading of the thermometer is taken and the hot wire is dropped through the valve into the charge which is at once ignited and burns completely in two or three seconds. The extraction of the heat is effected in about five minutes. The reading of the maximum temperature is taken and the calculations made as follows:

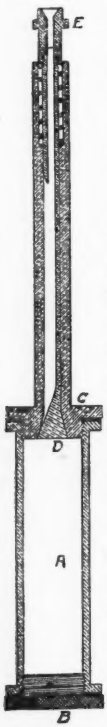

Fig. 2.

First.—A correction factor is needed for the hot wire. The average of many determinations on various lengths up to 2 inches establishes a fairly uniform factor of 0.012° C. or 0.021° F. per $\frac{1}{2}$ inch of No. 12 copper wire. In this work the lengths used have been $\frac{1}{4}$ inch and $\frac{3}{8}$ inch and the correction factor for the wire has been 0.006° and 0.009°.

Second.—A correction is made necessary by reason of the heat resulting from the combination of the products of combustion, carbon dioxide and water, with the chemical employed. This

heat of combination causes an excess over and above the actual heat of combustion, amounting to 27 per cent. of the total indicated heat. Hence, this correction must also be applied in the calculation. The method then of calculation will be as follows: Supposing a centigrade scale to have been used, if C′ represents the total indicated calories, C the actual calories due to combustion, t the rise in temperature, and w the water employed,

then $$C' = (t - 0.012^\circ) \times w,$$

and $$C = C' - \frac{C' \times 27}{100},$$

or $$C = (t - 0.012^\circ) \times w \times 0.73.$$

In case a Fahrenheit thermometer is used the temperature of correction for $\frac{1}{2}$ inch of wire is 0.021° instead of 0.012° and the final result is B. T. U. per pound of coal instead of calories. Of course with a centigrade thermometer the ultimate reading is changed from calories to B. T. U. by multiplying the calories obtained by 1.8.

A word of explanation is necessary as to the method of arriving at the factor for the heat of absorption of the products of combustion. The two elements concerned are carbon and hydrogen. For the carbon dioxide resulting from the combustion of the former, the correction factor is easily determined. Pure sugar carbon is prepared and run in the calorimeter as above described. The average of a number of such determinations gave a total calorific result of 11,084. Now taking as the accepted figure for the heat of combustion of carbon in calories, 8,080, we have therefore an increase of 3,004 calories due to the heat of absorption of the carbon dioxide by the chemical. By computation this is found to be 27.1 per cent. of the total indicated heat. Now as to the heat due to the absorption of water from the combustion of hydrogen the problem is not so simple. The burning of sugar affords no indication, for seemingly other compounds than water are formed and as in the case of sugar burned in the bomb calorimeter, while the results are constant and repeat themselves with exactness, they vary so widely from the theoretical data as to make it evident that the combinations do not proceed in a simple manner. Naphthalene does not afford a factor, chiefly owing to its volatility and consequent

faulty combustion. The liberation of a known weight of water in the interior of the cartridge gave very indifferent results, the water not disseminating throughout the peroxide but incrusting itself in a moist mass. Many other methods were tried with the result that so far at least it has been necessary to fall back on empirical data obtained from burning widely different varieties of coals and checking the same coals by combustion in standard bomb calorimeters. The following table gives the results thus obtained, using coals varying in their ash content from 3 to 32 per cent., and in water from 1 to 14 per cent. Also as wide a variation in the character of their hydrocarbons as possible, using a cannel coal,—Pennsylvania gas coal, a lignite and soft coals from widely separated districts in Illinois. Supposing the factor for absorption of water formed from a given weight of hydrogen to be approximately the same per cent. of total heat evolved as in the case of carbon dioxide, *viz.*, 27 per cent. and applying this factor throughout, we have the following results obtained by running parallel combustions in a standard Atwater or Mahler bomb calorimeter and the sodium peroxide apparatus. In a number of samples the process was conducted in both the Atwater and Mahler bombs. The instruments, however, checked so closely that this practice was not continued throughout the tests. The proximate analysis is included in the table in order that the wide variations in the character of the coals may be indicated (see table).

A few facts should be noted :

(*a*) It has been discovered after most tedious experience that a comparison of calorimeters should be made at approximately the same time. For example a series of calorific determinations made on finely ground samples on May 12, 1900, were found to give a reading 2.4 per cent. less on July 12, 1900. It was necessary to repeat practically all the above determinations on this account, all results showing a slow deterioration in the finely ground samples. This subject will receive further attention later.

(*b*) In the table it should be noted that the first five samples are from the same mine and vary but slightly in composition. The particular purpose in introducing this series was to note if

Kind of coal.	Proximate analysis.					B. T. U. per pound air-dried coal.		
	Moisture.	Volatile combustible.	Fixed carbon.	Ash.	Sulphur.	Bomb calorimeter.	New method.	Variation from standard bomb in per cent.
216 Carterville, Ill., mine run	4.87	34.11	52.17	8.85	0.85	12,205	12,214	+0.07
217 " " washed No. 1	4.66	33.99	54.21	7.14	0.74	12,289	12,286	0.00
218 " " " " 2	4.31	35.12	55.01	5.56	0.87	12,914	12,934	+0.08
220 " " " " 4	4.86	33.26	55.29	6.59	1.15	12,355	12,345	—0.08
221 " " dust from washer	5.50	32.97	53.01	8.52	1.16	12,384	12,336	—0.39
226 Odin, Ill., pea coal	7.27	35.76	42.96	14.01	3.89	11,025	11,064	+0.35
227 Farmington, Ill., mine run	11.22	35.93	36.60	16.25	3.98	9,986	10,018	+0.32
228 Pennsylvania gas coal	0.92	36.66	58.94	3.46	1.40	14,270	14,275	0.00
229 Kentucky cannel coal	0.99	32.33	34.35	32.33	1.07	10,313	10,328	+0.14
230 Mississippi lignite	14.56	43.82	29.30	12.32	...	8,316	8,378	+0.74

the calorimeter would differentiate between such small variations in the inert material, the ash and water.

Tabulating the results with reference to these inert materials and giving simply the calorimetric reading for each we have :

No.	Total of water and ash. Per cent.	B. T. U.
216	13.79	12,214
217	11.80	12,286
218	9.87	12,924
220	11.45	12,345
221	14.02	12,056

(*c*) It has already been mentioned but attention should again be called to the fact that with the calorimeter it is necessary to operate on the oven-dried sample for the reason that the water, if left in the sample, gives off heat in combining with the chemical; hence, a gram sample is weighed and dried in the oven or if the per cent. of moisture is known, an oven-dried sample may be weighed out, making allowance for the water. No other conditions vary the results. About 17 times the weight of coal is the best amount of peroxide to insure complete combustion but variations from 16 to 20 times the amount do not appreciably vary the results. Indeed with careful work and a good thermometer the instrument repeats its own results fully as closely as the bomb calorimeters. The usual practice, moreover, has been to work with half-gram samples, using a measured quantity,—8 to 9 grams of peroxide. With a suitable room and reasonable precautions as to temperature of both room and water employed, exceedingly constant and satisfactory results may be obtained which should vary less than 0.5 per cent. from the best figure obtainable with a standard instrument.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 28.]

ON THE DETERMINATION OF PHOSPHORIC ACID AS PHOSPHOMOLYBDIC ANHYDRIDE.

BY H. C. SHERMAN AND HENRY ST. JOHN HYDE.

Received July 23, 1900.

ALTHOUGH a great amount of work has been done in this country upon the subject of phosphorus determination, practically no attention seems to have been given to methods

which involve the ignition of ammonium phosphomolybdate and weighing of the residue. A given weight of phosphoric acid yields about sixteen times as much phosphomolybdic anhydride as magnesium pyrophosphate, and the "yellow precipitate can be ignited much more quickly and apparently with quite as definite results as it can be dried. It seems strange, therefore, that less attention has been given to this than to the other rapid gravimetric methods.

The first attempt to determine phosphoric acid as phosphomolybdic anhydride was probably that of Meineke.[1] The phosphate was precipitated by means of the ordinary acid molybdate reagent from a solution containing 20 to 25 per cent. of ammonium nitrate, heated to 50°–60° and vigorously stirred. After washing with a weakly acid solution of ammonium nitrate, the precipitate was heated below redness for fifteen minutes. The residue was believed to be of constant composition and to it was assigned the formula $P_2O_5.Mo_{24}O_{68}$.

Hanamann[2] about ten years later published a method very similar to that of Meineke but recommended that the precipitation be made at room temperature.

Later Meineke[3] made an extended series of determinations on solutions of pure phosphates from the average of which he calculated the percentage of P_2O_5 in the residue to be 3.949 per cent., agreeing well with the formula, $P_2O_5.24MoO_3$. He recommended that in the presence of a little iron the precipitation be carried out at 50° in the presence of 5 per cent. of ammonium nitrate, using the ordinary acid molybdate solution while if the solution contained much iron at least 10 per cent. of ammonium nitrate and 5 to 10 per cent. of strong nitric acid should be present and the precipitation carried out at a higher temperature. Good results are reported on two samples of phosphate.

Woy[4] developed the following method and applied it to a variety of technical products:

Reagents.—(1) A 3 per cent. solution of ammonium molybdate; (2) ammonium nitrate solution—340 grams per liter; (3) nitric acid of 1.153 sp. gr.; (4) wash solution containing

[1] *Repert. anal. Chem.*, **5**, 153 (1885); *Ztschr. anal Chem.*, **26**, 636 (1887).
[2] *Chem. Ztg.*, **19**, 553 (1895).
[3] *Ibid.*, **20**, 108 (1896).
[4] *Ibid.*, **21**, 441 and 469 (1897).

200 grams ammonium nitrate and 160 cc. of nitric acid in 4 liters of water.

Procedure.—To an aliquot part of the solution corresponding to 0.5 gram substance, add 30 cc. ammonium nitrate solution and 10 to 20 cc. of the nitric acid and heat until bubbles commence to rise, then add the necessary quantity of molybdate solution heated to the same degree (about 80° in our experiments). The reagent is run into the middle of the solution which is kept in motion during the operation. After fifteen minutes when the precipitate has settled, the solution is decanted through a porcelain Gooch crucible, the precipitate washed by decantation with 50 cc. of the wash solution and then dissolved in the beaker in dilute ammonia and reprecipitated by adding hot nitric acid, drop by drop, stirring or shaking the solution. Filter on the porcelain Gooch crucible and wash with the hot wash solution. Finally place the porcelain crucible inside of a nickel crucible and heat until the bottom of the latter is dull red. After fifteen minutes the precipitate is transformed into $P_2O_5.24MoO_3$.

Pellet[1] considers the second precipitation of ammonium phosphomolybdate recommended by Woy to be unnecessary. Having seen only a brief abstract of his paper we do not know the nature of the experiments on which his conclusion is based.

Hanamann[2] suggests that contamination with silica is best avoided by carrying out the precipitation at a low temperature and in the presence of considerable free nitric acid.

Some preliminary trials with microcosmic salt solutions having given results quite favorable to Woy's method whether with or without a second precipitation, we were led to compare on a number of samples: (1) The well-known molybdate-magnesia method carried out according to the directions of the Association of Official Agricultural Chemists and here called the official method; (2) Woy's method as published; (3) Woy's method, omitting the second precipitation of ammonium phosphomolybdate. The samples tested were not only "mixed" fertilizers but nearly all of them were "composites" so that together they represent a large variety of fertilizer materials.

[1] *Rev. Chim. Analyt. Appl.*, v. (20), 405; Abs. *Analyst*, **23**, 25 (1898).

[2] *Ztschr. landw. Vers-Sta. Ost.*, **3**, 53; Abs. *J. Soc. Chem. Ind.*, 378 (1900).

In each case solution was effected by boiling with 30 to 50 cc. of concentrated nitric acid and 5 to 10 cc. concentrated hydrochloric acid. The organic matter was not burned off before the solution nor was the silica removed by evaporation. The results obtained are shown in Table A which follows:

TABLE A. RESULTS WITH AND WITHOUT REPRECIPITATION.

No.	Description of sample.	Official method. Per cent. P_2O_5.	Woy's method: as published. Per cent. P_2O_5.	Woy's method: omitting 2nd precipitation. Per cent. P_2O_5.
1.	Mixed fertilizer	11.16	11.13	11.16
2.	" "	12.23	12.26	12.27
3.	" "	12.95	12.84	13.02
4.	" "	11.15	11.26	11.11
5.	" "	9.80	9.73	9.60
6.	" "	10.84	10.95	10.93
7.	" "	10.53	10.62	10.70
	Average	11.24	11.26	11.26

In these samples the second precipitation demanded by Woy's method seems to have been entirely unnecessary. We therefore tried the effects of salts of a few of the commoner acids and bases upon the results obtained by ignition of the first yellow precipitate. A commercial superphosphate was dissolved as above and its phosphoric acid content determined by the official method and by ignition of the first "yellow" precipitate. To aliquot parts of the same solution, corresponding to 0.4 gram of substance, were added the various salts, about 0.4 gram being used in each case. The yellow precipitate was ignited without reprecipitation. The determinations were not duplicated as in no case was the deviation from the true percentage greater than might easily be due to manipulation of a new method. The results are shown in Table B.

TABLE B. EFFECTS OF IMPURITIES.

Sample.	Method.	Per cent. P_2O_5.	Average.
Superphosphate.	Official method.	18.26	.....
"	Ignition of first yellow ppt.	18.14	18.20
" + $NaNO_3$	" "	18.16	.....
" + KNO_3	" "	18.10	.....
" + $Sr(NO_3)_2$	" "	18.31	.....
" + $Mg(NO_3)_2$	" "	18.21	.....
" + $Fe(NO_3)_3$	" "	18.15	.....
" + $Ba(NO_3)_2$	" "	18.33	.....
" + $(NH_4)_2SO_4$	" "	18.17	.....
" + NH_4Cl[1]	" "	18.10	18.19

[1] Woy found that very large quantities of ammonium chloride interfered with the precipitation of ammonium phosphomolybdate.

In carrying out the method it was naturally found that the precipitate formed was more granular and more easily washed if the molybdate solution was added very slowly and with vigorous stirring. The modification which follows seems to us to combine most of the best features of Woy's and Gladding's methods.

MODIFIED METHOD.

To the solution representing 0.2 to 0.5 gram of the sample, add 25 cc. strong ammonia (sp. gr. 0.90), neutralize with nitric acid and then add 5 to 8 cc., according to the impurities present, of concentrated nitric acid (sp. gr. 1.42) in excess. Bring the solution to a bulk of about 150 cc. and a temperature of 50° C. and maintain at this temperature (conveniently by standing the beaker in a pan of warm water) while adding, drop by drop with constant stirring, a neutral 3 per cent. solution of ammonium molybdate sufficient to give an excess of about 20 cc. Stir vigorously and allow to stand for about ten minutes; decant through a porcelain Gooch crucible and wash the precipitate three times by decantation with 50 to 70 cc. and then on the filter with 200 to 250 cc. of a cold solution of one part concentrated nitric acid in 100 parts of water. Finally the precipitate is ignited as described by Woy, leaving a residue of $P_2O_5.24MoO_3$.

Suction was employed in the filtration, and in washing on the filter the precipitate was well stirred up with the dilute acid wash solution. The neutral ammonium molybdate solution was employed simply to permit of the direct addition of the desired amount of nitric acid irrespective of the amount of the molybdate solution to be used.

As would be expected in working any new method, a few individual determinations were found on repetition to be wrong. These "wild" results were too high, doubtless from the precipitation of impurities, and emphasize the necessity of careful, slow addition of the molybdate solution. Only one sample was encountered in which the results obtained by the method described differed by more than two-tenths of one per cent. from those given by the official method. This was a phosphatic slag which contained, according to the official method, 17.27 per

cent. and according to the new method 16.97 per cent. of P_2O_5. The final precipitate obtained by the official method was, however, contaminated with iron and this result was thus undoubtedly too high, that by the new method being probably nearer the truth. These results on this sample are therefore omitted from the table which follows.

Table C below shows the results obtained by Woy's method, omitting the second precipitation, and by the modified method described above, together with the results obtained by the official method. The samples are numbered in the order in which they were analyzed.

TABLE C. COMPARISON OF RESULTS.

No.	Description of sample.	Per cent. P_2O_5 found. Official method.	Woy's method, omitting the second precipitation.	Modification of Woy's method, page 656.
1.	Mixed fertilizer	11.16	11.16	.....
2.	"	12.23	12.27	.....
3.	"	12.95	13.02	.....
4.	"	11.15	11.11	.....
5.	"	9.80	9.60	.....
6.	"	10.84	10.93	.....
7.	"	10.53	10.70	.....
8.	Acid phosphate	18.26	18.14	.....
9.	Mixed fertilizer	14.90	14.91	.....
10.	"	11.21	11.27	.....
11.	"	13.75	13.66	.....
12.	"	11.44	11.54	11.45
13.	"	17.55	17.57	17.42
14.	Steamed raw bone	32.34	.....	32.32
15.	Natural soft phosphate	20.80	.....	20.92
16.	South Carolina phosphate	27.60	.....	27.74
17.	Florida phosphate	29.76	.....	29.76
18.	South Carolina phosphate	27.92	.....	27.80
19.	Basic slag phosphate	17.77	.....	17.67
	Average, Nos. 1 to 13	12.75	12.76	.....
	Average, Nos. 12 to 19	23.15	.....	23.14

CONCLUSION.

In all of the twenty samples examined, which represent a large

variety of the common phosphatic materials of the fertilizer industry, the determination of phosphoric acid as phosphomolybdic anhydride was found to give satisfactory results even without a reprecipitation of the ammonium phosphomolybdate.

The presence in considerable quantity of some of the common acids and bases was found to be without appreciable effect.

With either modification of the method the average result obtained on all the samples analyzed was practically the same as that yielded by the official method which would seem to indicate that such variations as occur are due mainly to manipulation.

By the method described a determination may be completed in much less time than by any other gravimetric method with which we are familiar but in handling several samples simultaneously, the saving of time is less apparent.

COLUMBIA UNIVERSITY, NEW YORK CITY, July, 1900.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM ALCOHOLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

BY F. J. POND AND ARTHUR S. SHOFFSTALL.

Received August 1, 1900.

IN a preceding communication[1] on this subject it was mentioned that sodium methylate reacts with the dibromides of certain unsaturated ketones of the general formula,

$$R—CH=CH—CO—C_6H_5,$$

yielding 1,3-diketones of the formula,

$$R—CO—CH_2—CO—C_6H_5.$$

Thus benzylidene acetophenone dibromide was readily converted into *dibenzoyl methane*, and anisylidene acetophenone dibromide was found to give a 1,3-diketone analogous to dibenzoyl methane, and called *anisoyl benzoyl methane*. It was suggested that the formation of these diketones from the dibromides of unsaturated ketones was accomplished by the production of unsaturated ethers,

$$R—C(OCH_3)=CH—CO—C_6H_5,$$

[1] Pond, Maxwell, and Norman: This Journal, 21, 955.

which were converted by hydrolysis with dilute acids into the unsaturated ketone alcohols,

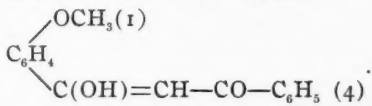
$$R—C(OH)=CH—CO—C_6H_5,$$

and these, in turn, by an intramolecular change into the saturated 1,3-diketones,

$$R—CO—CH_2—CO—C_6H_5.$$

Such a reaction would be somewhat analogous with the formation of ketones from the dibromides of anethol, isosafrol, and other propenyl compounds.

Closer investigation of the compound obtained from anisylidene acetophenone dibromide and of its derivatives leads us to believe that the last-mentioned change of the unsaturated ketone alcohol into the saturated diketone does not take place, and that the compound is a keto-enolic modification of anisoyl benzoyl methane and may be called *α-oxyanisylidene acetophenone*,



Its solution in alcohol is colored an intense brownish red by the addition of ferric chloride; aqueous ferric acetate, made by mixing the solutions of one part of ferric chloride and three parts of sodium acetate, throws out the ferric salt of α-oxyanisylidene acetophenone as a brick-red, crystalline precipitate, which is insoluble in water and alcohol, but soluble in dilute hydrochloric acid. W. Wislicenus[1] has suggested that the formation of such colored iron compounds on the addition of ferric chloride to the alcoholic solutions is a property of compounds containing the group,

$$C(OH)=C—,$$

such as phenols and the enolic modifications of β-keto-compounds; also, that in these colored iron compounds the metal is joined to the oxygen atom, a view which Claisen[2] also holds regarding the constitution of the iron salts of the β- or 1,3-diketones.

This compound is soluble in dilute alkalies, and is reprecipitated by acids. A green, crystalline copper salt is precipitated from its alcoholic solution by an alcoholic solution of copper ace-

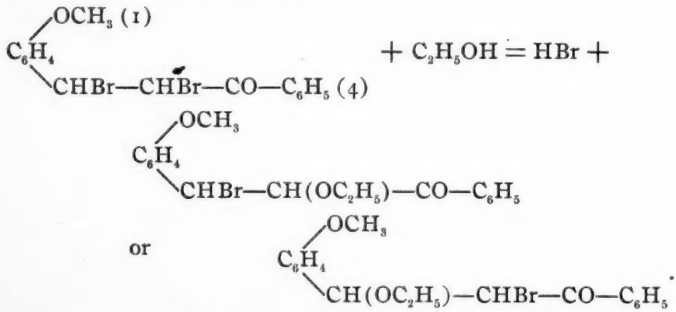
[1] W. Wislicenus: *Ann. Chem.* (Liebig), **291**, 174.
[2] L. Claisen: *Ibid.*, **281**, 344.

tate. It decolorizes immediately a solution of potassium permanganate in the cold, but it does not yield an additive product with bromine. It is indifferent towards acetic anhydride and benzoyl chloride.

The experimental part of our work is preceded by the following brief review of the contents of this paper.

The method of preparation of anisylidene acetophenone, the starting-point of our investigation, is slightly modified, by means of which a larger yield of the compound, melting at 78°, is obtained. This substance unites readily with two atoms of bromine, forming an additive product. The dibromide can not be recrystallized unchanged from alcohol, but it separates without change from acetic ether in large crystals, melting at 139° to 140°.

When anisylidene acetophenone dibromide is dissolved in alcohol and the solution is boiled for a short time, hydrogen bromide is eliminated and an alcohol addition-product of monobromoanisylidene acetophenone is produced :

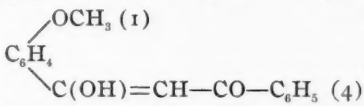


This is a saturated compound, which melts at 73.5° to 74.5°. When heated carefully in a distilling flask, no change is to be noted until the temperature reaches about 155° to 160°; a clear liquid then comes over having the odor and boiling-point of ethyl alcohol, and yielding the iodoform reaction. If the distillation be interrupted as soon as alcohol ceases to be given off, the liquid remaining in the flask solidifies and crystallizes from alcohol or ethyl acetate in large plates, melting at 94.5°; these are shown to be monobromoanisylidene acetophenone.

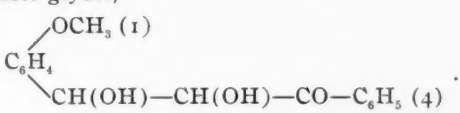
The analogous methyl alcohol addition-product was prepared,

and crystallized from methyl alcohol in fine crystals, which melt at 102°. The propyl alcohol addition-product is an oil, and is not further examined.

In a previous paper[1] it was shown that when anisylidene acetophenone dibromide was heated with two molecules of sodium methylate or ethylate and the resultant product hydrolyzed with hydrochloric acid, a compound was formed which melted at 131° to 132°; this compound was called anisoyl benzoyl methane. Further investigation has shown that it consists of α-oxyanisylidene acetophenone, *i. e.*, it is the α- or acid-modification of the diketone, $C_{16}H_{14}O_3$, and is to be represented by the formula,

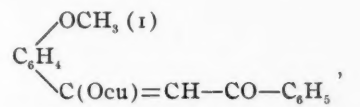


The filtrate obtained in the preparation of this compound yields an exceedingly small quantity of a silky, crystalline substance, which melts at 90° and is exceptionally soluble in alcohol; the analysis of this compound indicates that it has the composition represented by the formula, $C_{16}H_{16}O_4$. It may possibly prove to be the keto-glycol,



Until a method of preparation is found by which a suitable quantity of this substance can be obtained and further experimental evidence is secured, we do not care to commit ourselves regarding its structure. Should further investigation prove it to be the keto-glycol suggested above, its study will lead to very interesting results.

α-Oxyanisylidene acetophenone yields quantitatively a copper salt,[2]



which melts with decomposition at 247° to 249°. α-Oxyanisyli-

[1] *Loc. cit.*

[2] cu = ½ atom Cu.

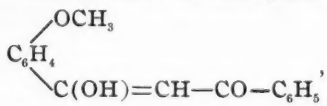
dene acetophenone is easily regenerated in a pure condition by warming this copper salt with dilute hydrochloric acid.

The action of hydroxylamine hydrochloride upon an alcoholic solution of α-oxyanisylidene acetophenone gives α,γ-methoxyphenyl-phenyl-isoxazole, melting at 120°; it crystallizes from alcohol in small flakes, which possess a brilliant mother-of-pearl luster. Claisen[1] has shown that monoximes of the β- or 1,3-diketones are not generally known. In attempts to prepare them, water usually splits off and an intramolecular anhydride formation takes place, giving the isoxazoles. J. Wislicenus[2] succeeded in preparing a monoxime from α-benzylidene acetophenone by the action of free hydroxylamine; but it showed a great tendency to lose water with the formation of α,γ-diphenyl-isoxazole.

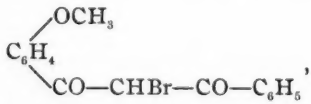
An isomeric methoxyphenyl-phenyl-isoxazole is formed by the action of an excess of potassium hydroxide upon the mixed alcoholic solutions of anisylidene acetophenone dibromide and hydroxylamine hydrochloride. It crystallizes from alcohol in small, silky needles, which melt at 128°.

Acetic anhydride and benzoyl chloride do not react with the hydroxyl group of α-oxyanisylidene acetophenone.

Bromine seems to convert α-oxyanisylidene acetophenone into a bromine derivative of the β-modification of the diketone. Instead of absorbing two atoms of bromine and yielding an additive product as would naturally be anticipated by the formula,



an atom of bromine is substituted for one hydrogen atom, and the compound,

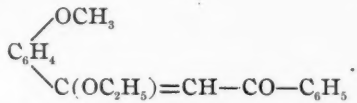


anisoyl benzoyl monobromomethane, is formed. It crystallizes well, and melts at 127.5° to 128.5°. It gives no coloration with ferric chloride and alcohol, and does not form a copper salt by

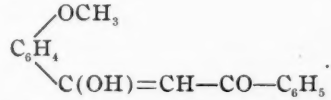
[1] L. Claisen: *Ber. d. chem. Ges.*, **24**, 3906; **21**, 2178; **24**, 390; **25**, 1787.
[2] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 250.

the addition of an alcoholic solution of copper acetate. It apparently contains no hydroxyl group.

An important part of our work is to determine, if possible, the exact course of the reaction by which the enolic-ketone is formed from anisylidene acetophenone dibromide by the action of sodium alcoholate. When one molecule of the dibromide is boiled with two molecules of sodium ethylate, the resulting product consists of an unsaturated ether,

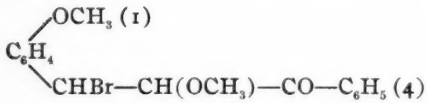


Dilute acids hydrolyze this compound with the formation of ethyl alcohol and the keto-enole,



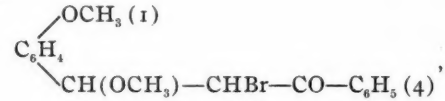
When sodium methylate is employed, the unsaturated methyl ether is produced, which also yields α-oxyanisylidene acetophenone on hydrolysis. The sodium alcoholate seemed to have a double action in that it split off one bromine atom as hydrogen bromide and then replaced the second bromine atom with the methoxyl or ethoxyl group. It therefore remained to determine whether the sodium alcoholate could react under certain conditions so that the two phases of the reaction could be separated, and the intermediate products isolated.

For this purpose we treated one molecule of the dibromide with a dilute solution of one molecule of sodium methylate in methyl alcohol. The product consists of two compounds: the one crystallizing in small needles and melting at 101.5° to 102.5° is the methyl alcohol addition-product of monobromoanisylidene acetophenone, and is formed in small quantity; the other is monobromoanisylidene acetophenone, which crystallizes in beautiful plates and melts at 94°. On heating the methyl alcohol additive compound it loses methyl alcohol and yields monobromoanisylidene acetophenone. This alcohol addition-product should probably be represented by one of the two following structural formulas,



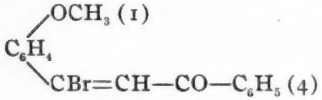
I.

or



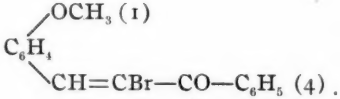
II.

and monobromoanisylidene acetophenone by the formula,



I.

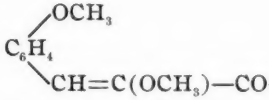
or



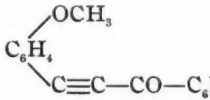
II.

For the present we prefer the formula I for each compound for the following reasons:

If the alcohol addition-product has the structure as represented by formula II, the unsaturated monobromide resulting from it by the elimination of methyl alcohol must have the formula II, thus containing the bromine atom in the β-position to the methoxyphenyl group. It would be expected that by the action of another molecule of sodium methylate upon this compound, a new ether,

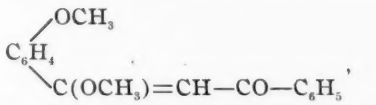


would be formed by the replacement of the bromine atom by methoxyl, or the monobromide might loose hydrogen bromide and yield a compound containing a triple linkage, benzoyl methoxyphenyl acetylene,



Neither of these compounds, however, have been obtained.

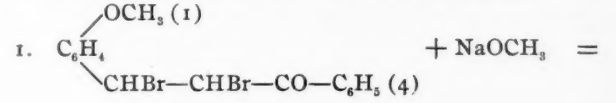
If the alcohol addition-product be represented by formula I, then by the splitting off of alcohol an unsaturated bromide having the above formula I with the bromine atom in the α-position would result. Such a compound might react with one molecule of sodium methylate giving rise to the same unsaturated methyl ether,

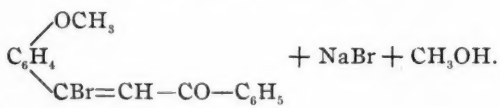


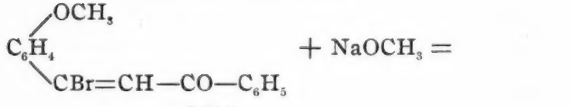
which is produced by the treatment of the dibromide with two molecules of sodium methylate, and by the hydrolysis of this ether the same keto-enole must result. Our experiments show that the reaction takes place in this manner, since the monobromide does react with sodium methylate, yielding the same ether which results by the action of an excess of methylate upon the dibromide, and from which α-oxyanisylidene acetophenone is formed by hydrolysis.

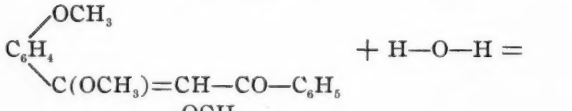
The formation of α-monobromoanisylidene acetophenone and of its alcohol addition-product in the same reaction would seem to indicate that one molecule of sodium alcoholate eliminates hydrogen bromide from a large part of the dibromide, yielding the unsaturated monobromide, and at the same time it replaces one atom of bromine in another smaller portion of the dibromide with the methoxyl group. It is also possible that, under the conditions of the experiment in which great care must be taken to avoid any excess over one molecule of sodium methylate, in order to prevent the elimination of both bromine atoms, that all of the sodium methylate is employed to remove hydrobromic acid, and that the small quantity of the methyl alcohol addition-product is due simply to the action of the methyl alcohol on some unchanged dibromide.

α-Oxyanisylidene acetophenone is probably formed by the action of sodium alcoholate upon anisylidene acetophenone dibromide in accordance with the following equations:





2. 

3. 

In the first phase of the reaction, the bromine atom in the β-position to the methoxyphenyl group is eliminated as hydrogen bromide with the formation of an unsaturated monobromide, while in the second stage, the bromine atom in the α-position is replaced by the methoxyl group, giving an unsaturated ether, which is readily hydrolyzed into the enolic ketone.

EXPERIMENTAL.

Anisylidene Acetophenone,

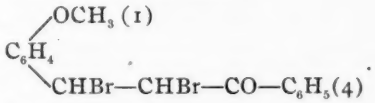
This substance is very readily prepared by the following method: Twelve grams of acetophenone and 13.6 grams of anisaldehyde (molecular proportions) are dissolved in 50 cc. of alcohol and treated with 5 cc. of a 20 per cent. solution of sodium methylate. After standing for about fifteen minutes, the solution is shaken vigorously for a few minutes, when the product separates as a yellow, crystalline solid; this is filtered by the pump, washed sparingly with cold alcohol, dried, and recrystallized from alcohol. It crystallizes from alcohol in long, light yellow

needles, and melts at 77° to 78°. It is easily soluble in hot ethyl and methyl alcohols, ether, and chloroform. Upon analysis it gave the following results:

I. 0.1582 gram gave 0.4674 gram carbon dioxide and 0.0822 gram water.
II. 0.1603 gram gave 0.4733 gram carbon dioxide and 0.0846 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found. I.	II.
Carbon	80.65	80.58	80.53
Hydrogen	5.88	5.77	5.86

Anisylidene Acetophenone Dibromide,



Twenty-five grams of anisylidene acetophenone were dissolved in 125 cc. of ether and the solution was cooled; 16.8 grams (one molecule) of bromine were added slowly and with constant shaking. After two-thirds of the bromine had been introduced, the product began to separate in fine, white crystals. The crystalline precipitate was filtered, washed well with cold ether to remove any slight excess of bromine, and dried on a porous plate. It was crystallized from ethyl acetate and obtained in thick prisms, melting with decomposition at 139° to 140°. It can not be recrystallized unchanged from ethyl or methyl alcohol; when dissolved in either of these solvents, hydrogen bromide is given off and crystalline compounds are formed, which will be subsequently described. It is readily soluble in acetic ether and crystallizes from it without evolution of hydrobromic acid; it is only sparingly soluble in ether.

It was analyzed with the following results:

I. 0.1807 gram gave 0.3228 gram carbon dioxide and 0.0567 gram water.
II. 0.1708 gram gave 0.3024 gram carbon dioxide and 0.0543 gram water.
III. 0.1669 gram gave 0.1566 gram silver bromide.
IV. 0.1825 gram gave 0.1738 gram silver bromide.

	Calculated for $C_{16}H_{14}O_2Br_2$.	Found. I.	II.	III.	IV.
Carbon	48.24	48.72	48.28	....	....
Hydrogen	3.52	3.49	3.53	....	....
Bromine	40.20	....	....	39.93	40.52

The Ethyl Alcohol Addition-product of α-Monobromoanisylidene Acetophenone, $C_6H_4\begin{cases}OCH_3\ (1)\\ CHBr—CH(OC_2H_5)—CO—C_6H_5\ (4)\end{cases}$.—It was noticed that when the preceding compound was crystallized from alcohol, considerable hydrogen bromide was given off and the resultant compound was quite different from the original dibromide. Fifty grams of anisylidene acetophenone dibromide were crystallized from ethyl alcohol and the resulting crystals were repeatedly recrystallized until they showed the constant melting-point, 74° to 75°. It is deposited from alcohol in long, white needles. It is unaltered by crystallization from methyl alcohol and by boiling its solution in methyl alcohol for several hours. It was dried *in vacuo*, and analyzed with the following results:

I. 0.1832 gram gave 0.4017 gram carbon dioxide and 0.0877 gram water.
II. 0.1822 gram gave 0.3969 gram carbon dioxide and 0.0872 gram water.
III. 0.1871 gram gave 0.0970 gram silver bromide.
IV. 0.1671 gram gave 0.0870 gram silver bromide.

	Calculated for $C_{16}H_{13}O_2Br$.	Calculated for $C_{18}H_{19}O_4Br$.	Found. I.	II.	III.	IV.
Carbon.....	60.56	59.50	59.80	59.41	....	....
Hydrogen...	4.10	5.23	5.32	5.32	....	....
Bromine	25.23	22.04	....	....	22.06	22.15

The analysis indicated that the compound was not the monobromoanisylidene acetophenone, $C_{16}H_{13}O_2Br$, at first anticipated, but that it was the ethyl alcohol addition-product of this bromide. It probably results from anisylidene acetophenone dibromide according to the following equation:

$$C_6H_4\begin{cases}OCH_3\\ CHBr—CHBr—CO—C_6H_5\end{cases} + C_2H_5OH = HBr + C_6H_4\begin{cases}OCH_3\\ CHBr—CH(OC_2H_5)—CO—C_6H_5\end{cases}\ \text{I.}$$

or

$$C_6H_4\begin{cases}OCH_3\\ CH(OC_2H_5)—CHBr—CO—C_6H_5\end{cases}\ \text{II.}$$

For the reasons suggested in the introduction we prefer formula I.

The substance behaves like a saturated compound. When it is dissolved in carbon tetrachloride it absorbs no bromine; the first drop of bromine added gives it a permanent red color, hydrogen bromide being evolved, and when one molecular proportion of bromine is added and the solvent evaporated, a crystalline substitution-product results.

The following experiment also indicates that it is an alcohol addition-product of α-monobromoanisylidene acetophenone.

Twenty-five grams of the substance (m. p. 74°) were heated in a distilling flask. It melted to a clear liquid which gradually assumed a yellowish color. At about 161° bubbles began to form and rise from the bottom of the flask, and a clear liquid distilled over. The temperature was further increased very slowly to 175°, when the distillation was interrupted. Two and one-half grams of liquid distillate were obtained having the odor of ethyl alcohol, and boiling at 77° to 78°; it yielded iodoform on treatment with iodine and potassium hydroxide, and was thus identified as alcohol. The yellow oil remaining in the flask was poured into a beaker, when it solidified at once, and was recrystallized from acetic ether; it separated in large plates, melting at 94.5°, and was proved to be α-bromoanisylidene acetophenone.

The same addition-product results on boiling the dibromide with alcohol in a reflux apparatus for several hours. Thus, 25 grams of anisylidene acetophenone dibromide were boiled with 200 cc. of alcohol on the water-bath for several hours, and the contents then allowed to crystallize. On recrystallization from alcohol, the product separated in long, white needles, which melted at 73.5° to 74.5°, and gave the following on analysis:

I. 0.1963 gram gave 0.1004 gram silver bromide.
II. 0.1230 gram gave 0.1187 gram silver bromide.

	Calculated for $C_{18}H_{19}O_3Br$.	Found. I.	II.
Bromine	22.04	21.76	21.95

An attempt to prepare monobromoanisylidene acetophenone by boiling an alcoholic solution of the dibromide with a molecular proportion of potassium acetate resulted in the formation of

the alcohol addition-product. Twenty-five grams of anisylidene acetophenone dibromide were dissolved in 200 cc. of alcohol and treated with an alcoholic solution of 6.2 grams of potassium acetate; after boiling for three hours, the resulting potassium bromide was filtered off at once. On cooling, a compound separated from the clear filtrate in long, white needles; these were recrystallized from alcohol, and melted at 73.5° to 74.5°. Analysis showed it to be the ethyl alcohol addition-product:

I. 0.2055 gram gave 0.1076 gram silver bromide.
II. 0.2008 gram gave 0.1044 gram silver bromide.

	Calculated for $C_{18}H_{19}O_3Br$.	Found. I.	II.
Bromine	22.04	22.23	22.12

The Methyl Alcohol Addition-product of α-Monobromoanisylidene Acetophenone, $C_6H_4<^{OCH_3\ (1)}_{CHBr—CH(OCH_3)—CO—C_6H_5\ (4)}$.

It was to be expected that a compound analogous to the preceding one would result on crystallizing the dibromide from methyl alcohol. Accordingly, 20 grams of anisylidene acetophenone dibromide were dissolved in hot methyl alcohol, the solution boiled for a few minutes and then allowed to crystallize. Hydrobromic acid fumes were given off during the boiling of the solution and continuously during the cooling. The resulting crystalline compound was repeatedly crystallized from methyl alcohol and obtained in the form of small, white needles, melting sharply at 102°. The compound is fairly soluble in methyl alcohol, and very soluble in acetic ether; it is also readily soluble in ethyl alcohol, and crystallizes from it, without change, in small needles, melting at 102°.

Analyses of the product recrystallized from methyl alcohol and dried *in vacuo* gave the following:

I. 0.1819 gram gave 0.3905 gram carbon dioxide and 0.0800 gram water.
II. 0.1818 gram gave 0.3887 gram carbon dioxide and 0.0800 gram water.
III. 0.2022 gram gave 0.1073 gram silver bromide.
IV. 0.1961 gram gave 0.1048 gram silver bromide.

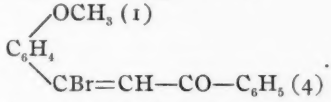
	Calculated for $C_{17}H_{17}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	58.45	58.55	58.31	....	....
Hydrogen	4.87	4.89	4.89	....	....
Bromine	22 92	....	....	22.58	22.74

This compound is the methyl alcohol addition-product expected. In attempting to distil it under diminished pressure, it suffered complete decomposition. When 25 grams were heated at the ordinary pressure, the substance melted to a clear liquid and, on raising the temperature to 160°, bubbles began to rise; from 167° to 180° a small quantity of a clear distillate was obtained, while the liquid in the flask had assumed a yellowish color. At 180° the heat was removed, and, on cooling, the contents of the flask solidified at once; this solid was crystallized from ethyl acetate and obtained in large, slightly yellow-colored plates, melting at 94°, thus showing it to be α-monobromoanisylidene acetophenone.

Anisylidene acetophenone dibromide dissolves in propyl alcohol with evolution of hydrogen bromide; on evaporation of the solvent, a colorless oil results, but it was not examined.

THE ACTION OF ONE MOLECULE OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

α-Monobromoanisylidene Acetophenone,



To a solution of sodium methylate, made by dissolving 1.5 grams of sodium in 125 cc. of methyl alcohol, was added 25 grams of the dibromide. The dibromide dissolved at once, forming a light yellow colored solution. After boiling for one hour, a small quantity of sodium bromide had separated and the solution was no longer alkaline to litmus. The sodium bromide was separated by filtration and the filtrate allowed to evaporate slowly. A product began to separate in large, yellow plates, and, after standing for some time, it was removed and the mother-liquor allowed to evaporate to dryness, when a second product, more soluble in alcohol than the plates, was obtained. The yellow plates were washed with water, pressed on a porous plate, and crystallized from acetic ether. The resulting crystals were again rubbed on a plate to remove oily impurities, and recrystallized first from alcohol and then acetic ether. The pure product separates from acetic ether in large, beautiful plates, which

are nearly colorless and melt at 94.5°. Its composition is shown by the analysis:

I. 0.1816 gram gave 0.4001 gram carbon dioxide and 0.0676 gram water.
II. 0.1873 gram gave 0.4125 gram carbon dioxide and 0.0680 gram water.
III. 0.1938 gram gave 0.1161 gram silver bromide.
IV. 0.1898 gram gave 0.1130 gram silver bromide.

	Calculated for $C_{16}H_{13}O_2Br$.	Found. I.	II.	III.	IV.
Carbon	60.56	60.09	60.06	....	....
Hydrogen	4.10	4.13	4.03	....	....
Bromine	25.23	....	....	25.49	25.33

This compound is, therefore, monobromoanisylidene acetophenone, and apparently constitutes the chief product of this reaction.

The second product, which is obtained by the evaporation to dryness of the methyl alcoholic filtrate as above mentioned, was pressed on a plate, since it contained some oil. It was then dissolved in acetic ether; plates of monobromoanisylidene acetophenone separated at first, and when the ether had nearly all evaporated, the second product was deposited in fine, white needles. A complete separation of the two compounds was made by fractional crystallization from acetic ether and then alcohol. The second product was purified by crystallization from alcohol, from which it was deposited in small, white needles, melting at 101.5° to 102.5°.

Analysis gave the following:

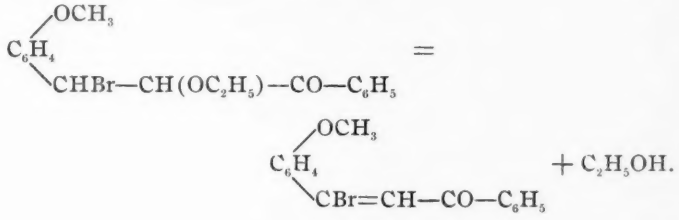
I. 0.1805 gram gave 0.3859 gram carbon dioxide and 0.0800 gram water.
II. 0.1808 gram gave 0.3874 gram carbon dioxide and 0.0825 gram water.
III. 0.2096 gram gave 0.1114 gram silver bromide.
IV. 0.2068 gram gave 0.1110 gram silver bromide.

	Calculated for $C_{17}H_{17}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	58.45	58.31	58.44	....	....
Hydrogen	4.87	4.92	5.07	....	....
Bromine	22.92	....	....	22.62	22.84

This substance is, therefore, the methyl alcohol addition-product of α-monobromoanisylidene acetophenone.

The α-monobromide is also readily formed by the action of one molecule of sodium ethylate on the dibromide. It is, however, best prepared by carefully heating the ethyl or methyl al-

cohol addition-products until the alcohol is removed, as was mentioned in the consideration of these compounds. It is purified by crystallizing from alcohol and then ethyl acetate, and forms large, well-defined plates, which melt at 94°. Its formation by the decomposition of the alcohol addition-products on heating may be represented as follows:



THE ACTION OF TWO MOLECULES OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

Fifty grams of the dibromide were added to a solution of sodium methylate, made by the action of 7.5 grams of metallic sodium on 150 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath, a reaction took place, the liquid became dark colored, and sodium bromide was deposited; the mixture was boiled for about one hour. On completion of the reaction, the sodium bromide was dissolved by adding 200 cc. of water, a dark colored oil, heavier than water, being thrown out. Twenty cc. of concentrated hydrochloric acid[1] were introduced, rendering the liquid acid and changing its color from brown to light yellow; it was then boiled for one-half hour, or until the oil was completely converted into a light yellow solid. After cooling, this was filtered off and the filtrate allowed to stand for several days, when another compound separated in very fine, white needles; this will be described in a subsequent part of this paper. The solid was washed well with water, dried, and crystallized from alcohol, in which it is spar-

[1] In other experiments it was determined that dilute sulphuric acid and even acetic acid also affect the conversion of the oil into the solid, giving identically the same product as concentrated hydrochloric acid. Carbon dioxide, however, does not affect this transformation.

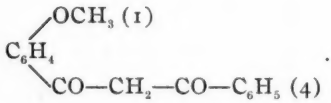
ingly soluble; it separated in fine, white crystals, melting at 130° to 131°.

The analysis gave the following:

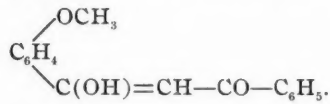
I. 0.2003 gram gave 0.5498 gram carbon dioxide and 0.1018 gram water.
II. 0.1981 gram gave 0.5424 gram carbon dioxide and 0.1001 gram water.

	Calculated for $C_{16}H_{14}O_3$.	Found. I.	Found. II.
Carbon	75.59	74.86	74.67
Hydrogen	5.51	5.65	5.61

This compound was first obtained by G. M. Norman and was previously described[1] as the 1,3-diketone, anisoyl benzoyl methane,



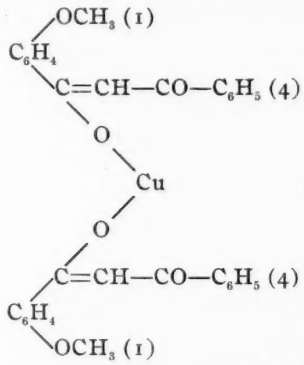
Its alcoholic solution is colored a deep violet-red with ferric chloride, and it is soluble in the hydroxides of potassium and sodium. Closer investigation, however, leads us to believe that this compound consists wholly, or at least for the most part, of the unsaturated ketone alcohol, α-oxyanisylidene acetophenone,



J. Wislicenus[2] obtained a mixture of α-oxybenzylidene acetophenone and dibenzoyl methane by the treatment of benzylidene acetophenone dibromide with an alcoholic solution of potassium hydroxide, and he found that the two substances could be readily and completely separated by the action of an alcoholic solution of copper acetate; the keto-enolic modification gave an insoluble copper salt, while the other remained unchanged in the alcoholic solution. This method of treatment with alcoholic copper acetate was applied to the above-mentioned substance (m. p. 130° to 131°) with the result that it was completely converted into a copper salt.

[1] Pond, Maxwell, and Norman: This Journal, 21, 966.
[2] J. Wislicenus: *Ann. Chem.* (Liebig), 308, 241.

Copper Salt of α-Oxyanisylidene Acetophenone,



The substance is formed when an alcoholic solution of the preceding compound is treated with alcoholic copper acetate. An alcoholic solution of 3 grams of copper acetate is added slowly and with vigorous agitation to the hot, alcoholic solution of 5 grams of the above compound (m. p. 130° to 131°). A fine, green precipitate of the copper salt separates almost immediately. The liquid above the precipitate remains colorless or slightly yellow until an excess of copper acetate is added, when it becomes green. It is essential that the liquid be kept near the boiling-point during the operation, otherwise the original compound separates. The precipitate is filtered and washed with alcohol until no trace of copper acetate is observed; it is further washed with water, then alcohol, and finally ether. It is insoluble in water, alcohol, ether, and carbon disulphide; very sparingly soluble in chloroform and benzene, and separates from the latter solvent in exceedingly small needles.

When the precipitated substance is purified by repeated washing with water, alcohol, and ether, it melts with decomposition at 247° to 249°. The analysis of such a preparation yielded the following figures:

I. 0.1984 gram gave 0.4868 gram carbon dioxide, 0.0832 gram water, and 0.0282 gram copper oxide.

II. 0.2386 gram gave 0.5850 gram carbon dioxide, 0.0955 gram water, and 0.0334 gram copper oxide.

III. 0.1825 gram gave 0.0257 gram copper oxide.

	Calculated for $C_{32}H_{26}O_6Cu$.	Found. I.	II.	III.
Carbon	67.41	66.92	66.86	....
Hydrogen	4.56	4.66	4.45	....
Copper	11.16	11.36	11.18	11.25

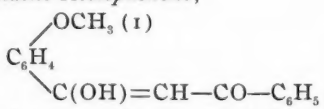
The formation of this copper salt is, therefore, represented by the following equation:

$$Cu(C_2H_3O_2)_2 + 2C_{16}H_{14}O_3 = Cu(C_{16}H_{13}O_3)_2 + 2CH_3COOH.$$

It consists of small, light green needles. It burns with a very smoky flame, leaving a residue of cupric oxide. Hot, dilute sulphuric acid decomposes it only very slowly, while hot, dilute hydrochloric acid readily converts it into cupric chloride and *α*-oxyanisylidene acetophenone; this reaction forms an excellent method of obtaining the latter compound in a pure condition.

The alcohol was distilled off from the combined green filtrate of the copper salt and the wash alcohol, and the residue extracted with ether. The excess of copper acetate was filtered, the ethereal solution dried, and the ether evaporated in a vacuum over calcium chloride. The residue consisted of a small amount of a dark, thick oil, which did not solidify after standing for two months, and decomposed on distillation under diminished pressure. No definite compound could be obtained from it.

α-Oxyanisylidene Acetophenone,



This compound was easily regenerated by boiling the copper salt for a short time with hydrochloric acid (1 : 3), and crystallizing the product from alcohol. It separates in small, yellowish white needles, melting at 130° to 131°, and boils at 284° to 286° under 44 mm. pressure, the distillate solidifying at once to an almost white, crystalline mass. The substance, purified by distillation and subsequent crystallization from alcohol, gave the following results on analysis:

I. 0.3009 gram gave 0.8309 gram carbon dioxide and 0.1501 gram water.
II. 0.2516 gram gave 0.6959 gram carbon dioxide and 0.1268 gram water.

	Calculated for $C_{16}H_{14}O_3$.	Found. I.	II.
Carbon	75.59	75.31	75.43
Hydrogen	5.51	5.54	5.60

It decomposes on distillation under atmospheric pressure. It is almost insoluble in cold alcohol, soluble in hot alcohol. It is easily soluble in chloroform, benzene, ethyl acetate, and carbon disulphide. Its alcoholic solution is colored a deep violet-red by ferric chloride, while ferric acetate precipitates the neutral iron salt of the keto-enole as a brick-red, crystalline substance, insoluble in alcohol and water. It readily forms the copper salt when treated with copper acetate and alcohol. Dilute nitric acid oxidizes it, forming a mixture of acids, probably benzoic and anisic. It dissolves in sodium and potassium hydroxide solutions and is reprecipitated with acids, melting at 129° to 130°. When the solution of the alkali is fairly concentrated and hot, the compound suffers decomposition into anisic acid, melting at 182° to 183°, and a ketone having an odor similar to that of acetophenone.

The Compound, $C_{16}H_{16}O_4$.—The filtrate obtained in the preparation of the crude α-oxyanisylidene acetophenone by the action of two molecules of sodium methylate upon anisylidene acetophenone dibromide was allowed to stand; after twenty-four hours, a white, silky, crystalline substance separated. After two weeks, when no further separation of crystals was observed, it was filtered, pressed carefully on a plate to remove oily impurities and repeatedly crystallized from alcohol. It is exceedingly soluble in alcohol, and it was found best in crystallizing to make a concentrated solution and then to place the dish in a freezing-mixture, when the compound is deposited in very fine, silky needles, melting at 90°. Its alcoholic solution is neither colored by ferric chloride nor precipitated by copper acetate. Its solution in benzene removes the color of a permanganate solution very slowly.

This substance is formed in an extremely small quantity. The analysis gave values required for $C_{16}H_{16}O_4$.

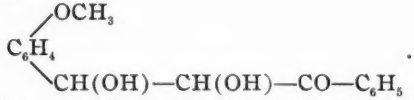
I. 0.1573 gram gave 0.4082 gram carbon dioxide and 0.0865 gram water.
II. 0.1441 gram gave 0.3736 gram carbon dioxide and 0.0794 gram water.

	Calculated for $C_{16}H_{16}O_4$.	Found. I.	II.
Carbon	70.59	70.77	70.70
Hydrogen	5.88	6.11	6.12

When one gram of the compound was boiled with an excess

of acetic anhydride for two hours, and the product poured into cold water, a thick, yellow oil separated. We were unable to isolate a definite compound from the oil.

Until a method of preparation is discovered by which a larger yield of this compound may be obtained, no satisfactory conclusions can be arrived at regarding its constitution. The analysis indicates the formula, $C_{16}H_{16}O_4$, and from its method of formation it is possible that the compound may prove to be the ketone glycol,



Owing to the want of material and limited time, the investigation of this substance was interrupted; the study of it will, however, be continued during the year.

THE ACTION OF SODIUM ETHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

The following experiments indicate that the product of the action of two molecules of sodium ethylate or methylate on the dibromide consists of the ethyl or methyl ether of α-oxyanisylidene acetophenone, which, on the addition of hydrochloric, sulphuric, or acetic acid, is converted into the corresponding alcohol and α-oxyanisylidene acetophenone.

Twenty-five grams of the dibromide were added to a slight excess over two molecules of sodium ethylate (4 grams of sodium in 100 cc. of ethyl alcohol), and heated for about two hours on the water-bath. All of the alcohol was then distilled off, water was added, and the solution rendered neutral to litmus by a few drops of acetic acid; the heavy oil, which separated, was taken up with ether, the ethereal solution washed repeatedly with water, dried with anhydrous sodium sulphate, and the ether distilled off. The residue consisted of a light red colored oil.

On standing, this oil is changed, crystals being gradually deposited, and, in the course of two or three weeks, a large part of the oil is converted into a crystalline mass. This change is accelerated by the addition of acids, and, indeed, strong hydrochloric acid causes the conversion to take place in a few seconds, dilute sulphuric and acetic acids reacting more slowly. The

solid is identified in each case as α-oxyanisylidene acetophenone.

This transformation of the oil into a solid is caused by the oil being readily hydrolyzed by the acids with the splitting off of alcohol and the formation of α-oxyanisylidene acetophenone, as is shown by the following: About 15 grams of freshly prepared oil were treated in the cold with 10 cc. of dilute hydrochloric acid (1 part acid to 1 of water); the oil solidified almost immediately, with a great evolution of heat. Twenty-five cc. of water were added, the solid was filtered, and the presence of ethyl alcohol in the filtrate was easily and distinctly recognized by the iodoform test. The solid crystallized from alcohol and melted at 128.5°; it gave the reaction with ferric chloride and copper acetate, and was identified as α-oxyanisylidene acetophenone.

The elimination of alcohol and the production of this solid indicates, without doubt, that the substance obtained by the action of two molecules of sodium ethylate on the dibromide contains an ethoxyl group, and we regard it as the *ethyl ether of α-oxyanisylidene acetophenone*, $C_6H_4\begin{cases}OCH_3\ (1)\\ C(OC_2H_5)=CH-CO-C_6H_5\ (4)\end{cases}$

When the dibromide is treated with 2 molecules of sodium methylate, in the same manner as above, an oil is obtained which remains unchanged for several weeks when kept in a tightly closed flask. On standing in an open flask, it is very gradually converted into a crystalline solid. When the oil is acted upon by dilute hydrochloric acid in the cold, it is quickly changed into a solid, with considerable elevation of the temperature. The solid is brittle and slightly yellow in color; it crystallizes from alcohol in small needles, melting at 129°, and is α-oxyanisylidene acetophenone. Although the oil could not be secured in a suitable condition for the analysis, it is exceedingly probable that the substance is to be regarded as the *methyl ether of α-oxyanisylidene acetophenone*,

$$C_6H_4\begin{cases}OCH_3\ (1)\\ C(OCH_3)=CH-CO-C_6H_5\end{cases}$$

The reaction of 2 molecules of sodium alcoholate upon anisylidene acetophenone dibromide appears to consist in first splitting off 1 molecule of hydrobromic acid with the formation of the unsaturated compound, α-bromoanisylidene acetophenone, and then in replacing the bromine atom in this compound with methoxyl or ethoxyl. The resulting unsaturated ether is readily hydrolyzed by acids with the production of α-oxyanisylidene acetophenone.

THE ACTION OF SODIUM METHYLATE ON THE ADDITION-PRODUCT OF α-MONOBROMOANISYLIDENE ACETOPHENONE AND ETHYL ALCOHOL.

Twenty-five grams of the addition-product were treated in the usual manner with 1 molecule of sodium methylate (2 grams of sodium in 100 cc. of methyl alcohol). On the completion of the reaction, 150 cc. of water were introduced, a dark colored oil being thrown out; hydrochloric acid was added until the liquid gave an acid reaction, and the mixture heated on the water-bath for a short time. The oil was rapidly converted into a solid, which was filtered and crystallized from alcohol; it melted at 129°, gave the color reaction with ferric chloride and alcohol, and a green precipitate with alcoholic copper acetate. It is α-oxyanisylidene acetophenone.

After standing during twenty-four hours, a small quantity of the compound, $C_{16}H_{16}O_4$, was deposited in long, slender needles from the filtrate obtained above; it melted at 89°.

THE ACTION OF SODIUM METHYLATE ON α-MONOBROMOANISYLIDENE ACETOPHENONE.

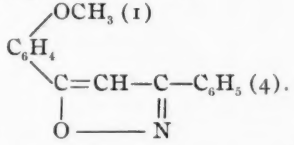
Fifteen grams of the monobromide were added to a solution of 1 molecule of methylate in methyl alcohol (1 gram of sodium in 75 cc. of methyl alcohol). After boiling for half an hour, the resultant sodium bromide was dissolved by the addition of water, the solution rendered strongly acid with acetic acid and heated for thirty minutes. On cooling, a crystalline substance separated, was filtered, and recrystallized from alcohol. It melts at 129.5°, reacts with ferric chloride and copper acetate, and is α-oxyanisylidene acetophenone. The yield of the enolic ketone was very good. A small quantity of the compound, $C_{16}H_{16}O_4$, melting at 89°, was deposited from the filtrate.

α-Oxyanisylidene Acetophenone and Acetic Anhydride.—Ten grams of α-oxyanisylidene acetophenone were boiled with 25 grams of acetic anhydride for eight hours, and the mixture then allowed to stand for forty-eight hours. On pouring the product into ice-water, a red oil, heavier than water, was produced; this was separated, washed with water, and allowed to stand. Since it did not become solid, it was taken up in alcohol, from which a substance crystallized in yellowish white needles similar to the original compound. It melted at 130° to 131°, reacted with ferric chloride and copper acetate, and appeared to be unchanged α-oxyanisylidene acetophenone. The acetate could not be isolated.

No better success was attained on treatment with benzoyl chloride, as in every case the unchanged material was obtained.

ACTION OF HYDROXYLAMINE HYDROCHLORIDE UPON α-OXYANISYLIDENE ACETOPHENONE.

αγ-Methoxyphenyl-phenyl-isoxazole,



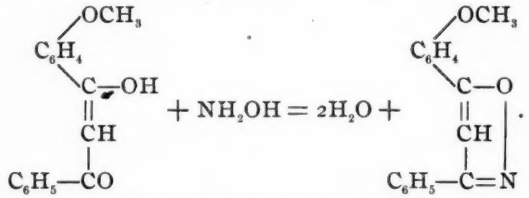
Five grams of α-oxyanisylidene acetophenone were dissolved in just enough hot alcohol to effect a solution in a small flask with reflux apparatus; 4 grams (3 molecules) of hydroxylamine hydrochloride were added, and the mixture was boiled gently during four hours. On cooling, a substance crystallized in beautiful, white crystals, resembling somewhat those of sulphocarbanilide. It was filtered, washed with water, dried, and crystallized from alcohol; it separated from this solvent in colorless, shining leaflets, which melted sharply at 119° to 120°. The following numbers were obtained upon analysis:

I. 0.1502 gram gave 0.4199 gram carbon dioxide and 0.0722 gram water.
II. 0.1935 gram gave 0.5422 gram carbon dioxide and 0.0914 gram water.
III. 0.7050 gram gave 39.2 cc. nitrogen at 23° and 726 mm.
IV. 0.6945 gram gave 39.4 cc. nitrogen at 24° and 726 mm.

	Calculated for $C_{16}H_{13}O_2N$.	Found. I.	II.	III.	IV.
Carbon	76.49	76.24	76.42	....	....
Hydrogen	5.18	5.34	5.25	....	....
Nitrogen	5.57	....	....	5.97	6.06

This compound is insoluble in water, alkali solutions, and dilute acids, difficultly soluble in cold alcohol, more readily soluble in hot alcohol and carbon disulphide, and very easily soluble in chloroform, ether, benzene, and ethyl acetate. Ferric chloride and copper acetate do not react with its alcoholic solution. It appears to be a very stable substance. It remains unaltered by boiling with a solution of potassium hydroxide. Concentrated hydrochloric acid dissolves it very sparingly, but is without further action upon it.

It is, without doubt, an isoxazole derivative, and results from the reaction of hydroxylamine upon α-oxyanisylidene acetophenone according to the equation,



It is probably analogous to the isoxazoles obtained by Claisen[1] by the action of hydroxylamine on the 1,3-diketones. J. Wislicenus[2] also obtained $\alpha\gamma$-diphenyl-isoxazole, melting at 140.5° to 141°, by the action of hydroxylamine hydrochloride on α-oxybenzylidene acetophenone. Goldschmidt[3] had previously produced a diphenyl-isoxazole, melting at 141°, by the reaction of an excess of sodium hydroxide on the mixed, warm, alcoholic solutions of benzylidene acetophenone dichloride and hydroxylamine hydrochloride.

It was, therefore, of interest to determinew hether the isoxazole above described or an isomeric compound would be formed by the treatment of anisylidene acetophenone dibromide with

[1] L. Claisen: *Ber. d. chem. Ges.*, **24**, 3906.
[2] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 249.
[3] Goldschmidt: *Ber. d. chem. Ges.*, **28**, 2540.

hydroxylamine hydrochloride and an excess of potassium hydroxide.

Isomeric Methoxyphenyl-phenyl-isoxazole, $C_{16}H_{13}O_2N$.—Twenty grams of anisylidene acetophenone dibromide are dissolved in 200 cc. of alcohol; to this is added a solution of 7 grams (2 molecules) of hydroxylamine hydrochloride in 10 cc. of water, and the mixture is heated to the boiling-point; 17 grams of potassium hydroxide in 20 cc. of water are then added very gradually, and with constant shaking, to the hot solution. A very vigorous reaction takes place with elimination of potassium salts, the solution assuming a yellowish red color. After standing for about ten minutes, the inorganic salts are filtered off, and on cooling the filtrate, a product separates in very fine, white needles. These are filtered, washed well with water, dried, and recrystallized from alcohol. It is deposited in very slender, silky needles, which melt at 127° to 128°.

The yield is further increased by precipitating the first alcoholic filtrate with water.

The analysis gave the following results:

I. 0.1887 gram gave 0.5282 gram carbon dioxide and 0.0894 gram water.
II. 0.1693 gram gave 0.4737 gram carbon dioxide and 0.0837 gram water.
III. 0.6972 gram gave 39.2 cc. nitrogen at 25° and 728 mm.

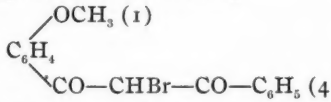
	Calculated for $C_{16}H_{13}O_2N$.	Found. I.	II.	III.
Carbon	76.49	76.34	76.31	....
Hydrogen	5.18	5.26	5.49	....
Nitrogen	5.57	....	....	6.00

This compound is soluble in alcohol, ether, carbon disulphide, and readily soluble in chloroform, benzene, and acetic ether. It dissolves, to a slight extent, in hot, concentrated hydrochloric acid, and is reprecipitated on the addition of water; cold, concentrated sulphuric acid dissolves it quite easily with almost no development of color, and when the solution is poured into water, the substance is thrown out apparently unaltered. Boiling potassium hydroxide solution is without action on the substance, and ferric chloride gives no coloration with its alcoholic solution, and copper acetate no precipitate.

This compound, melting at 127° to 128°, is probably isomeric

with the preceding isoxazole, melting at 119° to 120°, although its constitution is not yet definitely determined.[1]

Anisoyl Benzoyl Monobromomethane,



When α-oxyanisylidene acetophenone is dissolved in ether or chloroform and treated with one molecular proportion of bromine, hydrobromic acid is given off with gradual decoloration. On the evaporation of the solvent, a crystalline residue is obtained, which separates from alcohol in brilliant, white crystals, melting at 128°.

The analysis gave results corresponding to the formula, $C_{16}H_{13}O_3Br$.

I. 0.1784 gram gave 0.3790 gram carbon dioxide and 0.0655 gram water.
II. 0.1792 gram gave 0.3787 gram carbon dioxide and 0.0643 gram water.
III. 0.2062 gram gave 0.1158 gram silver bromide.
IV. 0.2060 gram gave 0.1166 gram silver bromide.

	Calculated for $C_{16}H_{13}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	57.66	57.94	57.64	....	....
Hydrogen	3.90	4.08	3.99	....	....
Bromine	24.02	....	....	23.89	24.08

It is soluble in alcohol, carbon disulphide, and ether; readily soluble in chloroform, benzene, and acetic ether.

Its alcoholic solution is not colored by ferric chloride, and gives no precipitate with copper acetate. It is probable, therefore, that the compound contains no hydroxyl group, and it may

[1] In an investigation which is being carried on in this laboratory, Mr. H. J. York has obtained the αγ-diphenyl-isoxazole described by J. Wislicenus (*Ann. Chem.* (Liebig), **308**, 249) by the treatment of α-oxybenzylidene acetophenone (resulting by the action of two molecules of sodium alcoholate upon benzylidene acetophenone dibromide and subsequent hydrolysis of the unsaturated ether with hydrochloric or acetic acid) with hydroxylamine hydrochloride. It crystallizes from hot alcohol in thick, colorless tablets, and melts at 141° to 142°. On treating benzylidene acetophenone dibromide in alcoholic solution with hydroxylamine hydrochloride and an excess of potassium hydroxide in a manner similar to the above, a compound resulted which was deposited from alcohol in thin, lustrous leaflets; these melted sharply at 140°. This compound contains nitrogen and is apparently identical with the substance described by Goldschmidt (*Ber. d. chem. Ges.*, **28**, 2540) as diphenyl-isoxazole. Although at the present time it is not proved that these two isoxazoles are different, the indications are that they are isomeric and not identical, and that they are analogous to the isoxazoles obtained from α-oxyanisylidene acetophenone and from anisylidene acetophenone dibromide.

be regarded as a bromine derivative of the neutral or β-modification of the diketone, anisoyl benzoyl methane.

We expect to continue this work in various directions, and to extend the investigations to other analogously constituted compounds.

A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF COPPER.

By S. W. Parr.

Received August 13, 1900.

EXPERIMENTS looking to the use of the thiocyanates in volumetric processes have been carried on in this laboratory for over two years past. While the results obtained are in many ways very satisfactory, it is intended here to make note of one application, which gives results of great practical value.

The iodine and cyanide methods for the estimation of copper are far from satisfactory. Two methods, recently proposed in this Journal,[1] making use of the precipitation of copper as cuprous thiocyanate, mark a decided advance in methods. It is believed that the process here outlined has further points of advantage. It involves the precipitation of the copper as cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acidified thiocyanate with standard permanganate. In practice the two latter steps are one operation, but one filtration is necessary and for most ores thirty to forty minutes are ample for a determination from the time of weighing the sample to the time of the final titration.

Some attention must be given to the condition of the solution before precipitating the copper as cuprous thiocyanate. If the solution contains free sulphuric acid it should not exceed 1 or 2 per cent. in amount. Stronger solutions on heating with thiocyanate have a tendency to liberate free sulphur which remains with the precipitate and in the final reading gives variable results. The same thing is true regarding hydrochloric acid. With nitric acid no free sulphur is liberated. Here, however, an excess of acid prevents the reduction and complete pre-

[1] This Journal, 19, 940 (1899) and 20, 610 (1900).

cipitation of the copper, so that in any case an amount of free acid in excess of 1 or 2 per cent. is to be avoided. Since the greatest safety seems to reside with the nitric acid it is preferred. This is an advantage also for in the initial treatment of mattes, ores, etc., it avoids the necessity of evaporating the solution to sulphuric acid fumes for the removal of the nitric acid. Further it may be noted that a small amount of sulphuric acid, resulting from the action of strong nitric acid or otherwise present, does not interfere with the precipitation. The reduction of the copper is best effected by a strong solution of sulphur dioxide, a few cc. being added from time to time. A 10 per cent. solution of sodium sulphite may be similarly used but it is better not to add acid to such a solution to liberate the sulphurous acid but allow it to be liberated by the free acid of the copper solution. The next point to be observed is the addition of the alkaline thiocyanate. The precipitated cuprous thiocyanate is very appreciably soluble in an excess of this reagent. Two cc. of a 10 per cent. solution of potassium thiocyanate will precipitate several times the amount of copper that could be conveniently handled in the subsequent titration; hence, that amount of reagent is sufficient to use, and at the same time there is no danger of re-solution of the precipitate. This reagent may be added with the reducing agent, before or after it, seemingly without preference. Heating on a water-bath or hot plate with stirring should be continued till the separation of the precipitate is complete and the supernatant liquid becomes perfectly clear. This requires from five to ten minutes.

The filtration is best made on a thick asbestos felt well packed in a 1½-inch porcelain filter funnel using a pump. A felt ⅛ inch or more thick should be used. The washing which should be made with hot water is complete when the filtrate, upon acidifying, will not decolorize a drop of permanganate. Special care should be taken that none of the precipitate passes through with the filtrate. The filter with the asbestos-pulp is returned to the beaker, 2 or 3 cc. of caustic soda (10 per cent.) solution are added, well stirred and warmed to 60° or 70°. The mixture after a few minutes is ready for titrating with the standard permanganate, the object being first to add to the alkaline mixture the amount of permanganate needed to oxidize the

cuprous hydroxide formed from the addition of the alkali, then to acidify and proceed with the rest of the titration to oxidize the thiocyanic acid. The first part of the reaction, that which takes place in the alkaline condition, is confined to the copper so long as any cuprous hydroxide remains. The following equation represents the change taking place:

$$8CuOH + K_2Mn_2O_8 + 8H_2O = 2KOH + 8Cu(OH)_2 + Mn_2(OH).$$

Now it is not necessary that at the exact end of this reaction on the copper the change should be made to the acid condition, but it is necessary that this point be fully passed in order that upon acidifying there may not be reprecipitated some cuprous thiocyanate. Fortunately it is easy to tell when this point has been passed, and in this way, when the copper has been all oxidized there begins a reaction between the alkaline thiocyanate and the permanganate which results in the formation of the green manganate thus:

$$4K_2Mn_2O_8 + NaCNS + 10NaOH = 4K_2MnO_4 + 4Na_2MnO_4 + NaCNO + Na_2SO_4 + 5H_2O.$$

It will be seen, therefore, that the bright yellow of the cuprous hydroxide becomes more and more mixed with the dark brown of the $Mn_2(OH)_6$ and soon fails to give any yellow tint whatever; further addition of permanganate produces a decided green tint to the liquid part of the mixture. If after a minute or two this remains permanent it may be known that all the copper has been oxidized.

Dilute sulphuric acid (1 : 5) is now slowly added with constant stirring to prevent heating. When the solution becomes clear a decided excess of the dilute acid is added, the whole warmed to 60° or 70°, and the titration continued to the usual pink end reaction. If in this part of the reaction the brown manganic hydroxide does not quickly disappear by solvent action of the acid, it is evidence that the acid is not present in sufficient excess or that the amount started with has been largely exhausted and more acid should be added. Concentrated acid may not, at any time, be added to the solution because of the tendency to form the carbon oxysulphide.

Notwithstanding the above somewhat roundabout reactions,

the whole process proceeds uniformly as if the reaction were simply thus: $10CuCNS + 7K_2Mn_2O_8 + 21H_2SO_4 = 7K_2SO_4 + 14MnSO_4 + 10HCN + 10CuSO_4 + 16H_2O$. This reaction serves to emphasize two things: first, that much sulphuric acid is needed in the reaction, and second, that the amount of permanganate used is high in proportion to the copper present.

This is further evident when it comes to the matter of calculation. In determining the permanganate factor for copper from its iron standardization it is noted that by the above equation the molecular ratios are: $10Cu : 7K_2Mn_2O_8$. Comparing with the usual iron ratio 1 : 10, we find the ratio between copper and iron to be 10Cu : 70Fe or 63.6 : 392 or 0.1602. Hence the iron value per cubic centimeter of the permanganate multiplied by the factor 0.1602 will give the copper value per cubic centimeter. While this feature is an advantage where the copper content is low, it also calls for the use of small quantities where the copper content is high, otherwise the consumption of permanganate will be excessive. It is therefore best to weigh out 1 gram of the substance and make up to 250 or 500 cc., and take an aliquot part as seems to be indicated by the depth of color due to the copper present. A decinormal solution of permanganate having an iron factor of 0.0056 would have a copper factor of 0.000897; hence, an amount of copper in excess of 40 milligrams would use more than 50 cc. of permanganate.

It may be well to note further that the amount of permanganate used in oxidizing the copper is only about one-sixth of the amount used in subsequent titration; hence, there is little danger of overrunning the total amount in the alkaline part of the process where the end reaction is indefinite. This point is further illustrated by the equation for thiocyanic acid alone, thus:

$$10HCNS + 6K_2Mn_2O_8 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O.$$

The process evidently demands that the thiocyanate precipitate be very complete, exact and free from sulphur. That these conditions are easily attainable seems to be indicated by the results. Removal of other metals is not necessary, even silver does not interfere because unaffected by the treatment with caustic alkali, and the insoluble silver thiocyanate acts so very

slowly on permanganate solution as not to vary the end-reaction appreciably. Results have been obtained as follows:

A solution of copper sulphate was made and acidified with nitric acid. Careful electrolytic determination of the copper gave a factor for each cubic centimeter of 0.00661 gram.

	Solution taken. cc.	Titration. cc.	Indicated copper in mg. per cc.	Error as referred to electrolytic result in mg. per cc.
(*a*)	5	32.8	6.63	+0.02
(*b*)	5	32.6	6.59	—0.02
(*c*)	5	32.8	6.63	+0.02
(*d*)	5	32.5	6.57	—0.04
(*e*)	5	32.7	6.60	+0.01
(*f*)	10	65.6	6.63	+0.02
(*g*)	20	130.6	6.59	—0.02
(*h*)	40	372.0	6.60	—0.01

The reaction between a thiocyanate and permanganate seems to be very constant. One exception only has been found and that not necessarily of such a nature as to interfere with the accuracy of the above process.

A solution of 1.5 grams of ammonium thiocyanate to a liter of water has a strength very nearly corresponding to N/10 permanganate solution. Now up to this point of dilution the thiocyanate seems to react regularly and in accordance with the above reactions. If, however, the thiocyanate be largely diluted beyond this point, the amount of permanganate used up in the reaction is appreciably less than the same quantity of thiocyanate would use, if undiluted. For example, a measured quantity, say 10 cc., of thiocyanate, if diluted 200 times, will titrate approximately 0.1 cc. of N/10 permanganate less than the same solution would use if undiluted.

This tendency to a lower titration seems to be corrected by acidifying more strongly with acid to correspond with the dilution; also in a less degree by somewhat higher heat.

Such possibility of error, however, is easily guarded against by keeping the solution of copper and thiocyanate in a concentrated form, or rather refrain from diluting the mixture, the necessary reagents alone furnishing all needed dilution from the time of treating the asbestos pulp and precipitate with alkali to the final titration with the permanganate. I desire to acknowledge my obligation to Mr. A. R. Johnston for the analytical data connected with this work.

UNIVERSITY OF ILLINOIS.

FREE ARSENIOUS OXIDE IN PARIS GREEN.

By E. W. Hilgard.

Received July 6, 1900.

In view of the many reclamations and conflicting results as to the content of free arsenious oxide in commercial Paris green that have reached this station since the publication of Bulletin No. 126, in which the unsatisfactory quality of the average material now on the market was discussed, it seems desirable to review briefly some of the causes of the discrepant results of different analysts.

The serious injury to foliage frequently resulting from the use of the commercial article led this Station to investigate specially the subject of the presence and correct determination of free As_2O_3. It should be understood that in the arid climates, where practically no rain falls during the summer, the absence of the periodic washing-off of the leaves, such as frequently recurs in the region of summer rains, permits of injury from a much smaller percentage of the free arsenical compound. The limit above which such injury occurs was found by our experience to be 4 per cent. of free arsenious oxide; and whenever that amount is exceeded we recommend the addition of a certain proportion of slaked lime to counteract its effects.

The New York law requiring the total percentage of arsenious oxide in Paris green to be "not below 50 per cent.," wholly omits any reference to the free or combined state of the compound. Hence some manufacturers have discarded all care in this respect, and greens containing as much as 20 per cent. and more, of the free oxide, are of frequent occurrence. Such articles are extremely objectionable in this climate at least, and probably elsewhere. This law certainly needs amendment, as it puts a premium on careless manufacture, or fraud. In some samples submitted to us it was evident that the "white arsenic" had been added in bulk to the green, as in the case of other adulterants, among which gypsum, Glauber's salt, chalk, and pipe-clay were easily identified by the microscope as well as by chemical tests. Microscopic examination proved, in fact, to be such a convenient and decisive test in most cases, that it is

always the first thing we do, as it frequently renders any further chemical work wholly unnecessary. The cogency of the microscopic examination is not so generally appreciated by chemists as it is by mineralogists; but there is no excuse for any mistakes in such work, as the crystalline forms of adulterants are perfectly conclusive, either directly, or after solution and evaporation. Especially can there be no mistake about the lustrous, sharp octahedrons of arsenious oxide, whether they be scattered about among the globules of Paris green, or, as is most commonly the case, adherent to the surface of the latter; so that in case of large proportions of the free arsenic, the globules are set with sharp octahedrons like a circular stone-saw or "diamond-drill." In most of such samples we have found the bulk of the free arsenic to be in this condition.

Such crystals dissolve very slowly in cold water, and even when 40° or 50° C. is used; and as a high temperature disintegrates the green globules, it does not seem admissible to employ it. After twenty-four hours' treatment with indefinite quantities of cold water, the arsenical crystals were sometimes still discernible as transparent, obtuse ridges around the outside of the globules, still constituting quite one-half of the total free arsenious oxide.

It is thus obvious that by treatment of Paris green for a few hours, with such small amounts of water as we find are in use at some of the Eastern stations (100 to 300 cc. per gram of green), too low results must be obtained. As in orchard practice the proportion of water used is from 500 to 1000 times the weight of the green employed, it seems proper to conform the analytical practice to this practice, in order to obtain results that shall represent the actual facts of the case. This is what we have adopted as a rule, together with the prolonged agitation of the green with the water, which is likewise practiced in the orchard. It is from this cause, doubtless, that our results are almost uniformly above those of our Eastern colleagues; but I think we are justified in adhering to what is manifestly in accordance with the practical outcome. It has been repeatedly said to us, in reply to our insistence on the microscopic examination, that "no Eastern chemist practices it." To this I have only to say, that in this as in numerous other cases, the microscopic examination usually affords so much more prompt and decisive informa-

tion regarding purity or adulteration than mere analysis, that I cannot but regard its omission as a serious mistake, in neglecting important evidence so readily obtainable.

It has been suggested that we do not take into account the "solubility of Paris green in water," as estimated from the amount of copper going into solution. But as in several cases we have found verdigris to pass into the first filtrates, the dissolution of copper being reduced to a mere trace when the washing was continued beyond 1000 cc. per gram, it is manifest that this correction cannot be applied safely without special precautions, even if it were certain that Paris green is soluble; in any case, the arsenic that passes into solution in this form cannot exceed a fraction of 1 per cent. In the case of a sample containing somewhat less than 4 per cent. of free arsenious oxide, for which an Eastern chemist has reported only 0.9 per cent., we found in the first 1200 cc. applied to 1 gram of substance, 0.26 per cent. of copper, for which, supposing it to represent Paris green, a similar weight of arsenious oxide would have to be deducted. But an additional 600 cc. failed to give *any* reaction for copper, even when concentrated to 25 cc., although a small amount of arsenic still continued to come. The microscope showed the cause of this continued slight contamination to be a few readily recognizable octahedrons of arsenious oxide adherent to the surface of the globules, here and there. Practically the same results were obtained by a slow percolation of cold water, when after the passage of 2000 cc. no copper reaction could be found; but a trace of arsenic continued to come through at the end of the fifth liter of water. In the sample thus washed, however, no arsenical crystals could be detected by the microscope, but only fragments of crushed globules of Paris green, whose form and aspect cannot be mistaken for arsenious oxide by any practiced eye.

It is thus obvious that extraction with a few hundred cc. of water for a few hours cannot yield a proper measure of the free arsenic present in Paris green. Not less than 600 cc., and preferably not less than 1000 cc., or 1 liter per gram, should be employed, and the extraction continued for twenty-four hours.

As to the test prescribed by at least one Eastern station, *viz.*, the solubility of the pure green in ammonia, it is utterly illusory

so far as "white arsenic" is concerned. Even if the latter were not itself rather readily soluble in ammonia, the fact stated in all books of reference that it is easily soluble in ammonium arsenite (which is of course formed when Paris green is dissolved in ammonia) fully disposes of any claim of this test to acceptance.

UNIVERSITY OF CALIFORNIA, June 30, 1900.

A METHOD OF DETERMINING FREE ALKALI IN SOAPS.

BY R. E. DIVINE.

Received July 26, 1900.

THE usual method of making this determination prescribes a separation of caustic from carbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering and washing the undissolved carbonate with alcohol and dissolving in water to titrate the solutions containing caustic and carbonate, respectively, with standard acid. This method is open to several objections, aside from the amount of time consumed. If it is desired to obtain accurate results on the caustic and carbonate separately, the preliminary drying of the soap introduces an error since the caustic alkali will take up carbon dioxide from the air unless the drying is done out of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if one is not provided with appliances to keep the funnel hot during filtration. Dudley and Pease[1] use an alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolved carbonate, and determine the latter in the usual manner. In the following process the writer has succeeded in eliminating filtration. For this method it is necessary to provide three standard solutions:

1. Hydrochloric acid, N/10 (for standardizing 2).
2. Caustic soda, N/10, in alcohol.
3. Stearic acid, N/10, in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthalein indicator.

Two grams soap (which needs no drying) is weighed into a round-bottomed flask, of about 300 cc. capacity, and 50 cc. alcohol poured upon it. N/10 stearic acid is now run in from a

[1] *Engineering and Railroad Journal*, (1891), 551.

burette in amount judged to be sufficient to neutralize the free alkali in 2 grams of the soap, some phenolphthalein added, and the flask then stoppered with a cork stopper, through which passes a glass tube about 30 inches long and of about $\frac{1}{4}$ inch internal diameter, the lower end ground to a point on a grindstone, and the purpose of which is to serve as a reflux condenser. The flask and contents are placed on a steam-bath and heated thirty minutes, at the expiration of which time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the color disappears, then several cubic centimeters in excess, and heat twenty minutes further. The flask is now removed from the bath and, after a few minutes' cooling, titrated with N/10 caustic soda. The difference between the number of cubic centimeters stearic acid solution added and the number of cubic centimeters caustic soda used to back titrate is equivalent to the total free alkali present.

While the first flask is heating, weigh out in a similar flask 2 grams of soap and add 50 cc. alcohol and place on the steam-bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask an amount of 10 per cent. barium chloride solution sufficient to precipitate alkali found,[1] heat a few minutes, add phenolphthalein, and titrate with N/10 stearic acid. The titration must take place slowly and with thorough agitation of the liquid for the reason that the sodium or potassium hydroxide reacts with the barium chloride added and forms sodium chloride and barium hydroxide. The latter is not very soluble in the alcoholic liquid and sufficient time and pains must be taken to ensure its complete neutralization by the stearic acid. A blank test should be made on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and the number of tenths cc. N/10 caustic soda necessary to neutralize the free acid in this quantity of alcohol added to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimeters N/10 stearic acid used to neutralize the caustic alkali in 2 grams of soap. The difference between the total

[1] 1 cc. N/10 stearic acid = 0.0122 gram $BaCl_2.2H_2O$ or 0.122 cc. 10 per cent. barium cholride solution.

alkali found and the caustic will, of course, give the carbonate. For example: 2 grams of soap and 15 cc. N/10 stearic acid; run in 3.2 cc. N/10 caustic soda to back titrate. Consequently, 15 — 3.2 = 11.8 cc. N/10 stearic acid equivalent to total free alkali.

To neutralize the caustic in the sample treated with barium chloride was required 4.1 cc. N/10 stearic acid. Fifty cc. of the alcohol used required 0.2 cc. N/10 caustic soda, then 4.1 + 0.2.

4.3 cc. N/10 stearic acid to neutralize free caustic alkali.

11.8 — 4.3 = 7.5 cc N/10 stearic acid to neutralize carbonated alkali.

1 cc. N/10 stearic acid = 0.004 gram caustic soda or 0.0053 gram sodium carbonate.

The above figures calculated to percentage would be:

0.86 per cent. caustic soda and 1.99 per cent. sodium carbonate.

It is to be noted that a rubber stopper cannot be used in the flasks for dissolving the soap on account of the sulphur in the rubber, which decolorizes an alcoholic solution of phenolphthalein. The method is applicable to all soaps which do not contain fillers which react with the standard solutions employed.

BUFFALO, July 24, 1900.

INVESTIGATIONS ON THE DETERMINATION AND COMPOSITION OF HUMUS AND ITS NITRIFICATION.

BY CHARLES RIMBACH.

Received July 30, 1900.

THE investigation on the nitrification of the *matière noire* of Grandeau, here discussed, was undertaken on the suggestion of Prof. Hilgard, to test the question whether or not that substance is to be regarded as a source of nitrates under the influence of nitrifying bacteria as has been assumed, but never definitely proved. The method of preparation consists in treating the soil with dilute hydrochloric acid to remove the lime and magnesia with which the humus substance forms insoluble compounds; and after washing with distilled water, until the filtrate is neutral, extracting it with 6 per cent. ammonia. On evaporation the solution leaves the *matière noire* behind.

As a medium containing the carbonates of lime and magnesia is most favorable to nitrifying bacteria, the compound of the

humus with these metals was employed for the experiment in order to simplify conditions. For this purpose the ammonia extract from a soil was precipitated with hot solutions of gypsum and magnesium sulphate ; the compound, which settles very slowly, was washed and decanted several times with gypsum solution to keep it flocculated, and then put on a linen filter. After the liquid had passed, the mass was further washed by shaking up in a bottle with gypsum solution, this operation being repeated until the filtrate was nearly colorless. The precipitate was dried at 100°, whereby it lost considerably in volume, forming a hard, brilliant, brittle mass with conchoidal fracture. It was free from ready-formed ammonia expellable by magnesia. The lime-magnesia compound thus prepared naturally contained gypsum. In the air-dried condition the precipitates prepared from two different soils had the following composition :

West Berkeley Soil.—An excessively stiff clay or "black adobe" soil, rich in lime, containing over 2 per cent. of *matière noire*.

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water	17.95
Ash	14.34
Organic matter	67.71
Nitrogen	3.06 of the organic matter.

Redwood Soil.—From Marin County (sandy humus soil).

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water	17.80
Ash	15.37
Organic matter	68.57
Nitrogen	4.01 of the organic matter.

The ash of the latter was soluble in dilute hydrochloric acid, leaving an insignificant white residue. It contained :

	Per cent.
Lime	47.07
Magnesia	13.65
Phosphoric acid	6.15
Potash in noticeable quantity.	

The humate from the Redwood soil, being the richer in nitrogen, was used for the nitrification experiment. Twenty-eight grams humate = 22.8816 grams dry matter with 0.767 gram nitrogen, were mixed in a beaker with 2 kilos of sand taken from drifting sand dunes, a short distance from the ocean near San Francisco; it had been previously ignited, and freed from nitrates by leaching with hydrochloric acid and distilled water.

The material for infection was prepared from soil of the ten-acre tract, Southern California Experiment Station. This soil contains from 1,560 to 12,280 pounds of alkali salts per acre to the depth of 1 foot; up to 23 per cent. of these are nitrates = 0.062 per cent. of the soil. After having been freed from nitrates by washing with distilled water, it was shaken with water, and the turbid liquid filtered through linen; the above mixture was moistened with the filtrate.

The material was kept for two months at a temperature of about 25°. Every other day, with some interruptions, the sand was moistened so that the content of free water amounted to about 2 per cent., stirred up with a glass rod, and thus kept in a mellow, flocculated condition, to facilitate the access of the air. After that lapse of time the moistened sand was mixed thoroughly, and a part of it was dried, weighed, and leached with water. The extract, subjected to the colorimetric determination of nitric acid, showed that 5.94 per cent. of the nitrogen of the humus substance had been nitrified.

Further experiments are in progress for comparing the nitrification in a natural soil, and in the same freed from *matière noire*, in which the microscope showed only slightly browned vegetable débris.

Conclusions.—The assumption made heretofore by Prof. Hilgard and others that Grandeau's *matière noire* is a direct source of nitrogen through nitrification, is definitely verified by the above experiment, in which all other possible sources were eliminated. It also justifies, presumptively, Prof. Hilgard's thesis that humus containing a high percentage of nitrogen, such as is found in the soils of the arid regions, will yield larger amounts of nitrates in the same time than will that of lower nitrogen percentages; and that conversely, low nitrogen percentages may fail to supply a sufficiency for plant growth.

Determination of Humus.[1]—An investigation was also made to test the Grandeau method for the determination of humus, and particularly that of nitrogen in humus, as hitherto used. The method is the following :

Two portions of 5 or 10 grams of air-dried soil are weighed off into prepared filters. They are treated with 1 per cent. hydrochloric acid to dissolve out the lime and magnesia, as already explained. The treatment with acid is continued until there is no reaction for lime ; the acid is then washed out with water to neutral reaction. The funnels containing the washed soils are now stoppered and one of them is treated with ammonia water (6 per cent.) for the determination of humus by evaporation, and the other with sodium hydroxide (4 per cent.) for the estimation of nitrogen. The lye, whether ammonia or soda, remains in the respective funnels a few hours ; the solution is then allowed to pass through and the filter washed once with the lye ; the funnel is then restoppered and a fresh quantity of the solvent put on the filter. The treatment is repeated until the filtrate remains colorless. The solutions are then made up to 1 liter, and aliquot parts are taken for the determination.

The ammonia solution is evaporated in a weighed platinum dish, the residue dried at 100°, weighed, ignited, and reweighed, the loss in weight showing the amount of humus.

The soda solution is treated with sulphuric acid and mercuric oxide to determine the nitrogen in the usual way.

The percentage of nitrogen in the sodium extract is referred to the percentage of humus in the soil as determined by ammonia extraction, for obtaining the percentage of nitrogen in the humus.

It was to be decided whether, as assumed in this method, ammonia and soda extract the same quantities of humus and nitrogen ; *i. e.*, the same substances. For this purpose two soils, peaty soil from Westminster, Orange Co., Cal., with 19.12 per cent. humus, and heavy black adobe soil from the University grounds with 1.20 per cent. humus, were treated as above described. A duplicate of the Westminster soil served for determining the quantity of humus lost for the analysis by the extrac-

[1] The word "humus," as used in this paper, is intended to designate Grandeau's *matière noire.*

tion with hydrochloric acid and water, which was prolonged until 1 liter of filtrate was obtained. Three hundred cc. of this filtrate on evaporation gave 0.0375 gram residue, containing 0.0367 gram organic matter with 7.45 per cent. nitrogen. This quantity of organic matter is 4.53 per cent. of that contained in the ammonia extract.

For determining the organic matter of the ammonia solution, aliquot parts of it were evaporated. The residue always contains combined ammonia, which was determined in another aliquot part (previously boiled to expel free ammonia) by distillation with magnesia. The quantity found, subtracted from the loss of weight by ignition, gives the organic matter. In the residue from the distillation the organic nitrogen was determined by the Kjeldahl method.

	Gram.
Residue of 200 cc. ammonia solution	0.1795
Ash	0.0108
Ash-free ammonia humate	0.1687
Less combined ammonia	0.00834
Organic matter	0.16036

The combined ammonia taken up from the ammonia solution amounts to 4.93 per cent. of the ash-free ammonia humate; the organic nitrogen, to 6.98 per cent. of the organic matter.

The determination of the organic nitrogen in the ammonia and soda solutions respectively, when applying the above correction, gave the following results:

	Mg.
Organic nitrogen in 100 cc. ammonia solution	5.33
Organic nitrogen in 100 cc. soda solution	8.23

These results are important in that they prove that soda solution extracts more nitrogen than does ammonia.

On account of the impossibility of determining the organic matter in the neutralized soda solution by evaporation and calcination, because of the large quantity of sodium salt, which hinders the combustion, it was decided to determine by the precipitation of the humus, the quantity and quality of humus-substances in both extracts. In order to determine which reagent precipitates the humus most completely, ammonia-humate extract from University adobe soil was treated with solutions of copper and magnesium sulphates, and with hydrochloric acid. Before adding the salt solutions, the humus

extract was freed from uncombined ammonia by boiling; the precipitates were washed with boiling water, in which the magnesium humate was rather soluble, while the filtrate from the copper humate was perfectly clear and nearly colorless. The hydrochloric precipitates were washed with 2 per cent. hydrochloric acid until 500 cc. had passed. All precipitates were free from ammonia. The nitrogen content of the filter was considered. For all precipitations the same quantity of ammonia extract was used.

	Precipitants used.		
	Copper sulphate.	Magnesium sulphate.	Hydrochloric acid.
Organic matter of the precipitates in per cent. of the total organic matter of the extracts	89.16	65.16	85.21
Nitrogen of the precipitates in per cent. of the organic matter of the precipitates	....	4.48	4.93
Nitrogen of the precipitates in per cent. of the total organic nitrogen of the extract	....	....	88.24
Ash in per cent. of the precipitates	23.40	14.60	5.21

These results show that magnesium sulphate (because of the solubility of humates in water) is not suitable as a precipitant, while copper sulphate precipitates the humus-substances most completely. Hydrochloric acid has nearly the same complete effect as copper sulphate, and as it can be added to the extract without previous elimination of ready-formed ammonia, it was used for the determinations described above.

The precipitation of the humus with hydrochloric acid in the ammonia and soda extracts from the Westminster and University soils, gave the following results:

		Precipitate of the humus acids by hydrochloric acid.	Organic matter of the same.	Nitrogen of the precipitates in per cents of the organic matter of the precipitates.	Nitrogen of the precipitates in per cents of the total organic nitrogen of the extract.
Westminster Soil—	cc.	Gram.	Gram.		
Ammonia solution	200	0.1127	0.2110	5.84	54.78
Soda solution	200	0.1495	0.1490	3.75	22.78
University Soil—					
Ammonia solution	300	0.0299	0.0233	....	....
Soda solution	300	0.0103	0.0077	....	....

It is thus seen that the humus-substances of these two soils behave altogether differently toward ammonium and sodium hydroxides as solvents.

The nitrogen of these precipitates was not determined on account of the small amounts obtained. The organic matter of the hydrochloric acid precipitate from the Westminster ammonia solution is 70.24 per cent. of the total quantity of organic matter contained in the same.

Even if the chlorides of ammonium and sodium should influence differently the solubility of the precipitates, the ratio of the latter, which is 3 : 4 in the first, and 3 : 1 in the second case, shows that substances of different nature are thus obtained.

Organic Matter in the Soda Extract.—For determining approximatively the ratio of nitrogen and organic matter in the soda extract, a weaker solution, which, of course, may have a different solvent power, was used in the extraction. 140 grams of University adobe soil, after being extracted with hydrochloric acid and water (250 cc. of the latter contained 0.0133 gram organic matter) was treated during twelve hours with 1 per cent. soda solution, then washed with 0.25 per cent. soda-lye, this operation being repeated until 1 liter filtrate was reached. 50 cc. of this were evaporated, the residue ignited, a solution of ammonium carbonate added in order to convert lime and magnesia into insoluble carbonates, evaporated again, and the residue gently heated. Then the ash was extracted with water and the quantity of sulphuric acid necessary for neutralizing the soda determined by titration. With the same quantity of acid 50 cc. of the soda solution was evaporated. The residue dried, weighed, ignited, and reweighed showed the organic matter. The determination of nitrogen was made with an aliquot part.

For comparison, 140 grams of the same soil were treated with the same quantities of acid, water, and 6 per cent. ammonia, and the extract was analyzed in the usual way. The ash-free residue contained 5.88 per cent. of ready-formed ammonia.

	cc.	Organic matter. Gram.	Organic nitrogen in per cents. of the organic matter.
Ammonia solution.....	50	0.0589	4.73
Soda solution.....	50	0.0543	5.37

These figures, however, do not allow a definite conclusion as to the total amount of soluble humic matter in the soil ; for it was found that in the ammonia filtrates obtained at different times during the extraction (which lasted six days), the nitrogen percentages of the organic matter vary considerably. The differences in the percentages of combined, ready-formed ammonia are small.

AMMONIA SOLUTION FROM SOIL FROM THE TEN-ACRE TRACT.

	Organic nitrogen.[1]	Combined ammonia.[2]
Filtrate from the first four hours	4.90	6.75
Filtrate from the seventh and eighth day	9.35	7.26

Apparently the humus-substances that are poor in nitrogen are readily soluble in ammonia and consequently form the main part of the first extract, while the substance with higher nitrogen percentages are less soluble and need a longer time for entire extraction by ammonia, but are more quickly dissolved by soda.

CONCLUSIONS.

1. By leaching with hydrochloric acid and water a certain quantity of humus, varying in the different soils, is lost to the subsequent extraction with ammonia.

2. The content of nitrogen of the soda extract, being different from that of the ammonia extract, cannot be directly referred to the content of organic matter of the latter.

3. In the determination of organic matter and nitrogen in the ammonia extract, the quantity of combined ammonia must be considered, as has been described in the analysis of Westminster humus.

It is thus evident that the percentages of humus heretofore determined are too high, inasmuch as the combined ammonia, which is about 5 per cent. of the ash-free ammonium humate, has been erroneously calculated as organic matter. Furthermore, if all soils behave like Westminster soil, from which soda extracts about one and a half times as much nitrogen as does ammonia, the nitrogen percentages in humus as heretofore determined, even though they are referred to organic matter and combined ammonia, would be too high.

[1] In per cents. of the organic matter contained in the solution.
[2] In per cents. of the ash-free ammonia humates.

4. The question still remains whether soda or ammonia solution, and in what strength, satisfy best the requirements of a solvent for humus substance, regarded as the sum of organic substances, decomposed or not, that are immediately available for the plants.

After concluding this investigation, we received a publication of A. L. Emery entitled "Soil Humus: Some Sources of Error in Analytical Methods."[1] As to the absorption of ammonia by the humus solution, there mentioned, it is, as we have explained, at least partially a simple process of combination of the humus acids (liberated by hydrochloric acid from earth bases) with the ammonia; the quantity of the latter has been regularly determined by Prof. Hilgard for some time past, by distillation with magnesia (not lime, which decomposes organic nitrogen compounds). A question, however, still to be decided is whether the ammonia used forms amido-compounds with the humus substances during the digestion or evaporation.

NOTES.

The Brown-Taylor-Richards Method for the Microscopical Identification of Butter.—In the June number of the Journal appears an article by John A. Hummel on "Brown and Taylor's Official" method of identifying butter, with plates showing the appearance of butter, oleomargarine, and renovated butter, when viewed by polarized light. This is the first time the method used by the Bureau of Internal Revenue for identifying oleomargarine has been formally christened, and I would suggest, if the designation is to stand in chemical literature, the addition of the name of Mr. Richards, formerly microscopist of this office, to whom is due the credit for its adoption and successful employment as a field test for the past twelve years. His report on this subject will be found on page CLXII of the Annual Report of the Commissioner of Interval Revenue for the fiscal year ended June 30, 1888. Directions for the use of the form of (unmounted) microscope officially adopted and its polarizing attachments are given in Series 7, No. 9, revised, of the Regulations of the Internal Revenue Office, everything being simplified as much as possible, so that the test can be performed by

[1] This Journal, **22**, 285 (1900).

persons not specially skilled in microscopical manipulation. These regulations, which are in the hands of all internal revenue officers, contain plates prepared by Richards showing the appearance of oleomargarine when viewed by polarized light, presenting the same characteristics as are given by the plates in Hummel's article, except that no reproduction is made of the appearance of butter, since this is, practically, a blank field.

In regard to the use of this test to distinguish between fresh and renovated butter, the experience of this office would tend to substantiate strongly the claims for its value put forth by Hummel. The regulations above referred to recognize the fact that it is really a test for the presence of melted fat, and prescribe that all samples giving a doubtful appearance in the microscope shall be sent in to Washington for a chemical examination. Of those which proved to be butter when thus examined, about nine-tenths are renovated butter, showing a field more or less mottled when examined with crossed nicols. In fact the value of the method as a sorting test to discriminate between butter and oleomargarine has been seriously impaired of late years by reason of the large quantity of renovated butter which has found its way into the markets. This is mainly due, however, to the lack of skill on the part of revenue officers, few of whom have occasion to make frequent use of the instrument. To a person skilled in the use of the polarizing microscope, it is not difficult to distinguish between oleomargarine and melted butter, for it is seldom a sample of the latter is met with which gives the sharply defined, crystalline appearance of the field typical of most oleomargarine. In applying the method to the identification of renovated butter much care should be exercised, for, in my experience, most butters will show *some* variation in the field, due probably to a slight crystallization at some period in their production, and it is rare indeed to find a sample giving the uniformly blank field implied by Hummel's plate of "normal butter."

The method certainly deserves mention along with the tests given by Hess and Doolittle,[1] the best of which is the "spoon test" (the absence of froth in oleomargarine or renovated

[1] This Journal, **22**, 150.

butter when heated in an open receptable) which has been in use for the detection of oleomargarine for many years, and which is preferred by some revenue officers to the microscope test.

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The Analysis of Arsenical Insecticides.—Since sending my article[1] on "The Adulteration and Analysis of the Arsenical Insecticides" to press I have done still further work on the soluble arsenious oxide in Paris green, and find that although an extraction of 1 gram of Paris green with 500 cc. of water finally gives practically constant results, still a small amount of cupric oxide goes into solution at the same time, thus indicating that either the Paris green itself is soluble in cold water or breaks up slightly on treatment with this medium. I am inclined to think that this last assumption is the more likely, since the amount of copper oxide going into solution in the 500 cc. of water is not constant.

If we assume then that the Paris green breaks up, and that for a certain amount of copper oxide a corresponding amount of arsenious oxide goes into solution, the figure obtained for soluble arsenious oxide (without taking into consideration the breaking up of the Paris green itself) which we will call the *apparent* per cent. of arsenious oxide, will not represent the *actual* per cent. of arsenious oxide, but a determination of the copper oxide dissolved in the water will have to be made, and after calculating how much arsenious oxide this corresponds to, the resulting figure will be subtracted from the *apparent* per cent. of arsenious oxide, thus leaving the *actual* per cent. of free arsenious oxide in the green.

It is of course possible, even probable, that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do.

The determination of copper oxide is made by precipitating an aliquot portion of the 500 cc. of cold water extract with hydrogen sulphide, filtering, washing and drying the combined sul-

[1] This Journal, **22**, 568.

phides of arsenic and copper, burning the precipitate and filter with powdered sulphur, and finally weighing as the mixed oxide and subsulphide of copper. On ten samples of Paris green the following results were obtained:

No.	Apparent per cent. of arsenious oxide extracted.	Per cent. of copper oxide extracted.	Arsenious oxide corresponding to copper oxide extracted.	Actual per cent. of arsenious oxide in Paris Green.
1	5.81	0.80	1.50	4.31
2	9.69	0.55	1.03	8.66
3	4.60	0.70	1.31	3.29
4	4.60	0.60	1.12	3.48
5	4.11	0.65	1.21	2.90
6	3.63	0.50	0.94	2.69
7	7.75	1.35	2.53	5.22
8	6.54	0.70	1.31	5.23
9	10.65	0.45	0.84	9.81
10	5.57	0.90	1.69	4.88

J. K. HAYWOOD.

On Carborundum.—In a paper on carborundum (carbide of silicon), read at the World's Congress at Chicago in 1893, and published later in this Journal,[1] there appeared in the second paragraph the following statement:

"It is an American invention, having been discovered by Edward H. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles."

As a part of the discussion at the close of the paper, I asked the author if he was aware that an electric furnace precisely similar to the one he had described was fully protected by letters patent issued to Messrs. Eugene H. and Alfred H. Cowles, in 1884. I further asked him whether the author was aware that in 1885, the substance to which had recently been assigned the name carborundum, was made in the Cowles furnace, and that specimens of this material could be found in several museums throughout the country. The author disclaimed any knowledge of such a furnace, or that any such material had been produced prior to that produced by Mr. Acheson.

In the United States Circuit Court of Appeals for the Third Circuit (Judges Dallas, Gray, and Bradford), a decision has

[1] This Journal, 15, 411.

just been rendered (May 28, 1900) in a case of infringement, in favor of the patent granted to A. H. and E. H. Cowles, Dec. 24, 1884, and against the patent of E. H. Acheson, alluded to above.

In stating the ground of their decision, the judges make the following statement: "There can be no doubt on the evidence that prior to the process patent in suit metallurgical operations had been performed through the instrumentality of the electric arc, electrical conductors consisting of wires or rods of metals, or of other solid or concrete bodies, or by electrolysis. But on careful examination we have failed to find any patent, publication, or other matter alleged as an anticipation, or as showing the prior art, a practical process for metallurgical or analogous operations involving the use of a discrete body of conductive, but resistant material rendered incandescent by the passage of an electric current, and mixed or otherwise in contact with the material to be treated. This is the broad, underlying idea of the process patent in suit, and is covered by its claims. The Messrs. Cowles were the first to invent and use this process, and the patent must be sustained. It is a meritorious one, and its claims are entitled to considerable liberality of construction." This decision gives priority broadly to the Messrs. Cowles for reducing ores and other substances by the incandescent method.

CHARLES F. MABERY.

CLEVELAND, June 5, 1900.

NEW BOOKS.

THE CHEMISTRY OF THE METALS. By J. H. KASTLE. Lexington, 1900. vi + 198 pp. 8vo.

The author of this book admits in his preface that the number of text-books on general chemistry is so great that "the burden of proof certainly rests upon any new writer who ventures into this field to show that anything new in this line is deserving of publication," and makes a plea for the fuller study of the metals, bodies that constitute two-thirds of the elements. The author says: "An attempt has been made to supplement the laboratory work on each family of metals with a general presentation of the subject according to the Periodic Law."

Chapter I opens with general elementary statements as to the

differences between mixtures and compounds, analysis, synthesis, and chemical study of a substance; in successive chapters are given descriptions of the metals taken by families and by groups so as to avoid unnecessary duplication, extending from the alkalies to iron, nickel, and cobalt. Following the descriptive portion of each chapter are sections prescribing "Laboratory Work;" these sections consist chiefly of series of questions and in them lies the principal claim to originality for the volume. The queries are intended to make students think for themselves, but sometimes are singularly elementary; thus, following several pages describing the character of the metal magnesium, students are asked—"Is magnesium a metal?" "Is it heavy or light?" "What is its color?" (p. 47). After comparing granite and mercuric oxide, students are asked—"How could you make mixtures?" Yet some of the queries are difficult and would require examination of larger treatises.

To use this volume for instruction, the students must have previously become acquainted with the gaseous elements, the principal acids of inorganic chemistry and the rudiments of qualitative analysis, yet the primary principles of chemistry are laid before them with minutiae that would seem unnecessary had they mastered them previously. At the same time students are directed to make certain experiments, and the instructions given are hardly sufficient. On page 5, for example, students are told to heat HgO in a hard glass tube and to collect the gas evolved over water, but how to arrange this is not mentioned, nor is there any wood-cut of apparatus to illustrate the operation; indeed, illustrations are entirely wanting throughout the volume.

A blemish in the manufacture of the book is due to the carelessness of the printer; paper of uniform color and glaze is not used throughout; page 112 is of a bluish tint, and page 113 of a decided yellow hue. There is no index.

H. CARRINGTON BOLTON.

ERRATA.

In Vol. 22, page 573, line 23, for "sodium acetate" read "sodium arsenate;" page 576, line 28, for "really" read "nearly."